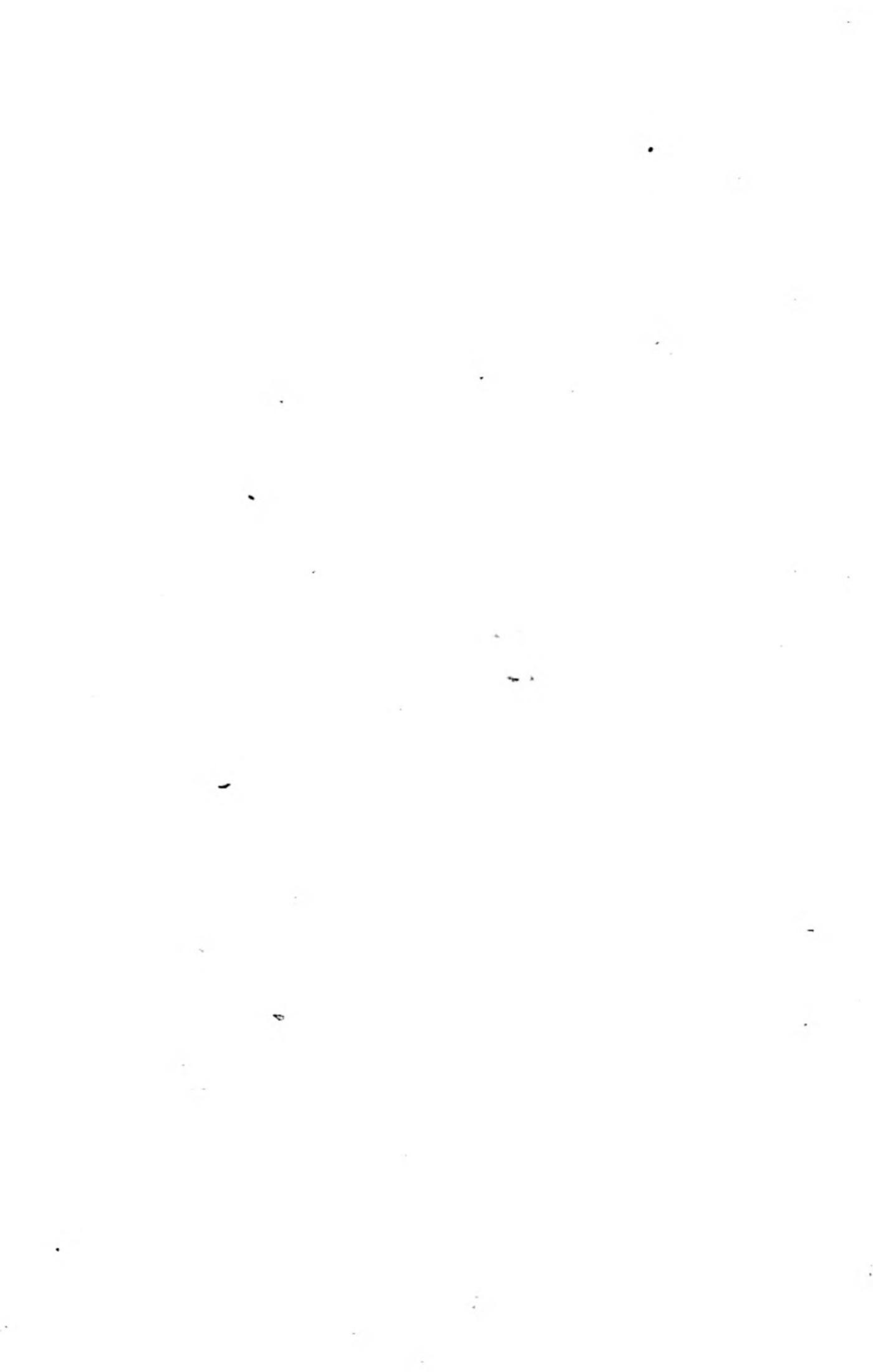
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NEW IDEAS

ON

INORGANIC CHEMISTRY

BY

DR. A. WERNER

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF ZÜRICH

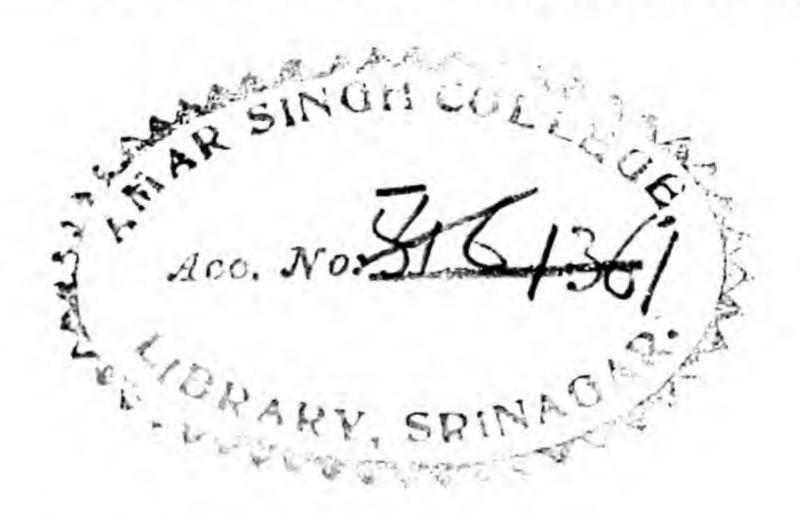
TRANSLATED, WITH THE AUTHOR'S SANCTION, FROM THE SECOND GERMAN EDITION

BY

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1911

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"To explain molecular compounds atomically, i.e. from considerations based on the capacity for saturation of the element, has become the chief problem of modern chemistry."

—BLOOMSTRAND, Chem. der Jetztzeit, 1869, p. 127.



DEDICATED

BY THE TRANSLATOR TO

WALTER NOEL HARTLEY, D.Sc., F.R.S.,

PROFESSOR OF CHEMISTRY, ROYAL COLLEGE OF SCIENCE, DUBLIN,

IN GRATITUDE FOR EARLY TRAINING AND MANY

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TRANSLATOR'S PREFACE

In presenting the accompanying translation of the presenting to English-speaking chemists, the translator hopes that he is thereby making Prof. Werner's book of greater use to them. The book is a veritable mine of suggestions for research on Inorganic Chemistry, and should this translation bring home to any one the great possibilities of research in this direction, then the translator has attained his desire.

In the present translation the incorrect formulæ which crept into the second German edition have been rectified, and the translator wishes to acknowledge his indebtedness to the author for his help in this direction. The author has added also some new references relating to work which has been published since the appearance of the German original.

E. P. H.

THE UNIVERSITY,

BIRMINGHAM,

February, 1911.

AUTHOR'S PREFACE

TO THE SECOND GERMAN EDITION

As compared with the first edition the present one has been to a great extent rewritten, and in part considerably extended.

The revision had for its chief object the reduction to an harmonious whole of the sections discussing the problem of valency. I hope that I have been able to bring out more clearly the relationships between the apparently very diverse conceptions of valency, and thus to lay the foundation upon which, in the near future, it will be possible to build a consistent doctrine of valency.

The enlargements which the book has undergone consist chiefly in the treatment of the different groups of compounds of higher order. By a more detailed consideration of the experimental material, I have tried to make manifest and illustrate the importance of the general point of view.

Further, some new sections (Theory of Bases and Acids, Theory of Hydrolysis, Constitution of Polynuclear Metallic Ammino-complexes, Theory of Inner Metallic Complex Salts) have been added as the fruit of the intervening years. I have endeavoured also, by making the references to the literature as complete as possible, to render the book useful for reference to workers in inorganic chemistry. On the whole, however, the book has preserved its original character, so that even in its revised form the theories which have been offered to explain experimental results still occupy the most prominent position.

A. WERNER.

ZÜRICH, November, 1908.

This book is beyond the scope

AUTHOR'S PREFACE

TO THE FIRST GERMAN EDITION

THE advances in our knowledge of inorganic chemistry make it increasingly evident that our conceptions of valency, which have been so greatly developed by the study of organic chemistry, cannot give an adequate picture of the constitution of the molecule of inorganic compounds. Consequently, attempts multiply to obtain, by enlarging the doctrine of valency, a broader theoretical foundation for the constitution of inorganic compounds. Even now it is possible to discern, though dimly, what form the new conceptions of valency and of the constitutions of inorganic compounds will assume. Such a knowledge, when finally attained, will teach us the general laws governing the compounds of the elements. It therefore appears useful to arrange, in a composite form, those principles which at present are of importance to our conceptions of the structure and configuration of inorganic compounds. In doing this, we fully recognize that our new theory is little more than a summary of the facts, and from which only just as much should be expected as from any other scientific hypothesis, i.e. as Mach puts it, the rendering possible of an economy of thought and description. Nevertheless, should these conceptions be replaced later by others more perfect, they may have served to pave the way for the systematization of the almost innumerable facts of inorganic chemistry. It is with this hope that I leave to the judgment of my scientific colleagues the following summary of the hypotheses which are of fundamental importance for inorganic chemistry.

A. WERNER.

Zürich, September, 1905.

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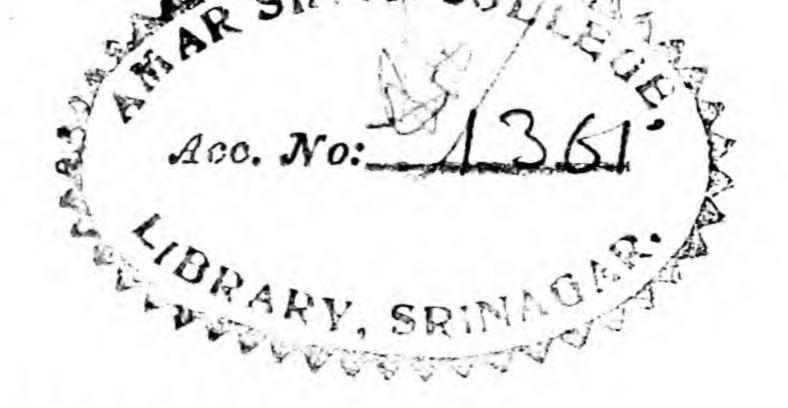
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I. The Elements.

1. The Conception of an Element.

ELEMENTS are homogeneous substances which defy decomposition by most of our analytical methods. This definition is reached by an exhaustive study of the properties and relations of the elements one with another. These relations are epitomized in the periodic system.

Modern chemistry postulates that the elements are different forms of one and the same kind of matter. This suggestion arises not from hypothetical considerations of the unity of matter, but from considerations based upon certain characteristic relations among the elements. That such relations exist may be ascribed possibly to the conditions under which the elements were formed, for they would be perfectly incomprehensible were it not supposed that they had a common origin. Researches, which appear to show the possibility of decomposing some of the elements, offer considerable support to this definition of an element.

The work of Ramsay has shown that the emanation from radio-active substances, according to the conditions under which it decomposes, yields helium, neon, or argon. Further, lithium salts are produced by the action of radio-active emanation on solutions of copper salts. The decomposition products which are produced successively from the original radio-active substance are characterized by definite "radio-active constants." The disintegration hypothesis is the outcome of the study of these radio-active bodies and postulates the spontaneous decomposition of radio-active elements into other elements. It would lead us too far were we to consider in greater detail this most interesting subject, and there is less necessity to discuss it here since there exist many good monographs on the subject.

Yet caution ought to be exercised before the disintegration hypothesis is accepted finally, for every scientific philosopher knows

how often incorrect deductions are made from quite simple practical data and unlimited experimental evidence. On this account it must be emphatically stated, that the researches on this subject, the experimental results of which are above criticism, cannot be considered as conclusively proving the decomposition of the elements, and a firmer foundation of our modern ideas on the relations of the elements to one another is greatly to be desired.

The conception of a meta-element, which is a variation of the idea of an element, at one time attracted attention, but has now been abandoned. In 1887, Crookes suggested that the elements were mixtures of substances the reactions of which were extraordinarily alike, and that the atomic weight of the element represented the mean of the atomic weights of the components. This view was the outcome of the great difficulties experienced in separating the constituents of the rare earths, but to-day has no experimental justification. The progress made in the chemistry of the rare earths has been so great that there is no longer any room to doubt that these mixtures, formerly considered to be inseparable, can be broken down into a small number of well-defined elements.

Oswald has given a new definition of an element from considerations based upon the phase rule. He defines the elements as substances which, under all known conditions, can only form hylotropic phases. This definition corresponds completely with the usual one, according to which elements are substances from which nothing different can be prepared without the addition of a new substance. It seems doubtful whether the deductions of the stoichiometrical laws, made by Oswald from this definition, will prove satisfactory.

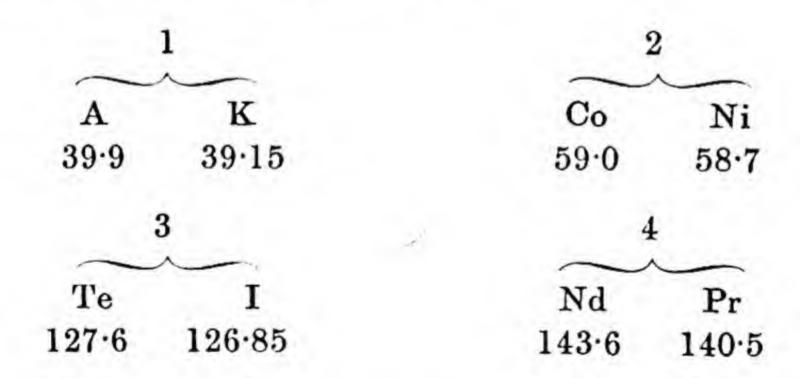
2. The Periodic System.

The most comprehensive system which gives expression to the properties of the elements is that which has been developed chiefly by Newlands, Mendelejeff, and Lothar Meyer. Nevertheless, it fails to call attention to all the analogies which exist between the elements, and on this account many new systems have appeared in which it has been attempted, by the rearrangement of Mendelejeff's and Lothar Meyer's tables, to bring into prominence a greater number of the inter-relations of the elements. These new systems endeavoured in particular to illustrate the theory that all the

elements are evolved from one primordial kind of matter. Attempts have also been made to overcome the difficulties experienced in placing the rare earths in Mendelejeff's and Meyer's systems. We do not intend to discuss the former difficulty, since as yet no definite result has been reached. On the other hand, the difficulties encountered in placing certain elements in the periodic system may be considered in order to indicate a way in which such difficulties may possibly be overcome. These difficulties are of two kinds. In the first place, they lie in the undoubted fact that the properties of certain elements are not those which are to be expected from their atomic weights and from their resulting position in the periodic system. The properties of these elements correspond rather to those of elements which should occupy either the foregoing or following position in the periodic table.

In the table facing p. 6 these elements are enclosed in brackets. These irregularities convey the impression that increase in atomic weight and periodic change of the properties of the element, while occurring together, are in no way connected with one another.

Up to the present such irregularities are only to be found at four places of the periodic system, viz.—



A closer examination of these four pairs of exceptions shows that they might be divided into two sub-groups, for cases 3 and 4 are the periodic repetition of cases 1 and 2. Case 1 (argon and potassium) comes at the end of the second period, and case 3 (tellurium and iodine) comes almost at the end of the fourth period. Six or seven elements after exception 1 (or 3) the second (or 4th) exception is repeated.

Both the latter pairs of exceptions are further characterized by the fact that their salts crystallize in red or green hydrates. The red cobalt salts correspond to the red salts of neodymium, while the green nickel salts correspond to those of praseodymium. Finally, it is noteworthy that the colours of the cobalt and nickel salts, or those of neodymium and praseodymium, are complementary. So that even the exceptions to the periodic system show a regularity amongst themselves.

To assign positions to certain newly discovered elements constitutes the second difficulty of the periodic system. The "noble gases" discovered by Ramsay are satisfactorily placed in a group contiguous to the halogens. This position has been assigned to them on account of the values obtained for their atomic volumes. On the other hand, up to the present, the satisfactory grouping of the metals of the iron group and of the rare earths appears to be almost impossible. Most of these difficulties are not difficulties of principle, i.e. they are not to be referred to the nature of the metal in question, but rather to that particular arrangement adopted to illustrate the periodic occurrence of chemically allied elements.

The principle chosen by Mendelejeff, of bringing analogous elements as near as possible together in order to bring out the less evident similarities which exist between such elements, has been followed by his successors. This procedure has led to a crowding together (Ineinanderschachtelung) of the elements which is harmful to the synoptical character of the periodic system, and this is especially true when we consider only the less important analogies: the result of equal valencies. This compression of the elements into the least possible space is the chief cause of many elements not finding a suitable position in Mendelejeff's scheme. This remark is particularly applicable to the so-called 8th group, and to the metals of the rare earths. It has always been felt that Mendelejeff's system was incomplete in this respect, and accordingly attempts have been made to overcome this insufficiency. Two such attempts have been published by H. Blitz 1 and B. Brauner.² These authors have grouped together certain elements, and placed this group in one of the large natural groups. The tables of Blitz and Brauner are appended.

¹ Ber., 35, 562 (1902).

² Zeitsch. anorg. Chem., 32, 1 (1902).

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ELEMENTS
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SYSTEM
PERIODIC

Series.	Group 0.	Group I.	Group II.	Group III.	Group IV.	Group V.	Group VI.	Group VII.	Group VIII.
	0	Φ	Φ	12	RH,	RH3	RH	RH	Highest hydrogen compound.
	R	R,0	RO	R,03	RO2	R.O.	RO3	R20,	RO, Highest oxide.
н		11							
63	He 4	Li 7	Be 9	B111	°C 12	N 14	0 16	F 19	First short period.
8	20 Ne	23 Na	24 Mg	27 Å	28 Si	31 P	32 S	35.5 CI	Second short period.
41	A 40 >	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	MN 55	Fe 56 Co 59 Ni 59 Cu 63.
2		68 Cu	65 Zu	70 Ga	72 Ge	75 As	79 Se	80 Br	First long period.
9	Kr 82	Rb 85	Sr 87	X 89	Zr 30	Nb 94	Mo 96	- 100	Ru 102 Rh 103 Pd 106 Ag 108
7		108 Ag	112 Cd	114 In	119 Sn	120 Sb	128 Tex	127 Y	Second long period.
œ	Xe 128	Cs 133	Ba 137	La 138	Ce usw.	Ta 182	W 184	- 190	Os 191 Ir 193 Pt 195 Au 197
6		197 Au	200 Hg	204 TI	207 Pb	209 Bi	212 -	214 -	Third long period.
10	- 218	- 220	Ra 225?	- 230	Th 233	≥ 235	U 239	Pus 4	Fourth long period.
11									

He	Li	Be	В	C	N	0	F
Ne	Na	Mg	A1	Si	P	S	Cl
A	K	Ca	Sc	Ti	v	Cr	∑ Fe
Kr	Cu	Zn	Ga	Ge	As	Se	Br
X	Rb	Sr	Y	Zr	Nb	Mo	∑Pd
	Ag	Cd	In	Sn	Sb	Te	I
	Cs	Ba	ΣCe		Ex		
			Yb		Ta	W	≥ Pt
	Au	Hg	Tl	Pb	Bi		
				mb		7.7	

PERIODIC SYSTEM OF THE ELEMENTS. (H. BLITZ.)

Sub-groups.

$$\Sigma$$
 Ce = La Ce Pr Nd; Σ Fe = Mn Fe Co Ni; Σ Pd = Ru Rh Pd; Σ Pt = Os Ir Pt.

Both these arrangements assign a special position to those elements which they group together, which does not give sufficient expression to their relations to the other elements, and in certain directions is contrary to the fundamental principle of the periodic law. The grouping together of the elements into groups can, on this account, be considered only as a makeshift, and, as already mentioned, is to be referred to the attempt to include too many analogies in the system. It therefore appears advantageous to omit the less important analogies from the natural system of the elements, and to consider only their chief characteristics. This treatment is all the more justified since it is possible for elements to resemble one another in their properties without a close relationship between such elements being necessary. Such broad fundamentals allow of a much less artificial survey of the elements, and consequently a much more satisfactory scheme is obtained. (See accompanying table.)

In the first place, such an arrangement shows that the system consists of a definite number of elements. These elements probably always occur in pairs of series, and the number of elements in each pair of series is always greater than the number in the preceding pair. Up to the present four different kinds of series can be recognised.

1. A very short one, containing only hydrogen and helium. 2 The lithium and sodium series, which correspond to each

other and contain eight elements apiece. 3. Two series, beginning with potassium and rhubidium, both containing eighteen elements. 4. Two which we can call the cesium and radium series. Of the latter only three elements, radium, thorium and uranium, are known, but the number of elements to be expected in this and the cesium series may be calculated by the following method. When the average increase in atomic weight of two consecutive elements in any series is estimated, the following results are obtained:—

Lithium Series . . .
$$20.0 - 7.03 = \frac{12.79}{7} = 1.85$$

Sodium Series . . . $39.9 - 23.05 = \frac{16.85}{7} = 2.4$
Potassium Series . . . $81.12 - 39.15 = \frac{42}{17} = 2.47$
Rhubidium Series . . . $128.0 - 86.04 = \frac{42.6}{17} = 2.5$

From these figures it is clear that the mean of the difference in the higher series undergoes a regular increase, it being smallest in the first series. It can, therefore, be deduced that in the hydrogenhelium series the mean difference is about 1.5, so that in this series it is very probable that an element is still to be expected, possibly the prototype of the negative elements. The hydrogen-helium series accordingly should consist of three elements, and, if it is accepted that each series occurs twice, it ought to be considered as the second of the shortest series of the periodic system.

The number of elements in the lithium and sodium series is eight, an increase of five elements over the previous series.

If the homologue of manganese, as yet unknown, is included, then the following two series consist, in each case, of eighteen elements. The numerical increase over the foregoing series is consequently ten, *i.e.* twice the increase of the lithium and sodium series over that of hydrogen.

The caesium series is incomplete, but, with the help of the differences deduced above, it is possible to forecast with a fair degree of probability the number of elements it ought to contain. For this series the average difference must be assumed as somewhat greater than that of the immediately preceding series. If we take it to be 2.56 and divide this number into the difference between the atomic weights of cæsium and bismuth

Bi Cs

$$208.5 - 133 = 75.5$$
 $\frac{75.5}{2.56} = 29$

we obtain twenty-nine as the number of elements in this series. The fourteen elements of the rhubidium series, i.e. Sb to Y and Sr, when subtracted from twenty-nine leaves fifteen as the number of new elements to be included in this series. These fifteen elements constitute the groups of rare earths.

When the number of elements in each pair of series are compared with one another, we arrive at the following results:—

1st unknown and 2nd Series (H (?) He) each contain 3 elements.

3rd and 4th Series $\left\{ \begin{array}{l} \text{Li-series} \\ \text{Na-series} \end{array} \right\} = \begin{array}{l} \text{each of 8 elements} \\ = 3 + 5. \end{array}$ 5th and 6th Series $\left\{ \begin{array}{l} \text{K-series} \\ \text{Rb-series} \end{array} \right\} = \begin{array}{l} \text{each of 18 elements} \\ = 3 + 5 + (2 \times 5). \end{array}$ 7th and 8th Series $\left\{ \begin{array}{l} \text{Cs-series} \\ \text{Ra-series} \end{array} \right\} = \begin{array}{l} \text{each of 33 elements} \\ = 3 + 5 + (2 \times 5) + (3 \times 5). \end{array}$

A comparison of these figures reveals the noteworthy fact that each pair of series differs from the others by a multiple of five. That the number of new elements to be included in the seventh series is about fifteen is deduced from the interval in the atomic weights between barium and the unknown homologue of yttrium.

Benedicks,1 on an atomic volume curve for the rare earths, has shown that these values increase regularly, beginning with cæsium and ending, as far as we know at present, with bismuth. The prediction regarding the number of elements to be expected in the seventh series therefore receives a certain amount of support. Moreover, this new arrangement of the elements shows that the higher and longer series are developed from the shorter by the insertion of intermediate elements. The properties of the latter alter so gradually that they almost seem as if they were variations of the two elements between which they are intermediate in position. Accordingly we find that of the intermediate elements of the fifth and sixth series—Cu, Ni, Co, Fe, Mn, Cr, Ag, Pd, Rh, Ru, and Os appear like variations of the metallic properties of zinc, while the others—Ca, Sc, Sr, and Y—in certain properties, e.g. the strongly basic character of their hydroxides, approximate to potassium. The difference between these two groups of elements finds

¹ Zeitsch. anorg. Chem., 39, 41 (1904).

further expression in their occurrence in nature; most of the former occur in the free state, while the latter are found only as oxides. The position, intermediate between potassium on the one hand and zinc and gallium on the other, which the elements occupy is again brought out in the type of compounds they form. Those which resemble zinc and gallium in the di- and tri-valent conditions form the same types of compounds as these two elements. Thus, for example, Va, Cr, Mn, Fe, Co, and Ni crystallize in isomorphic sulphates with the general formula MeSO₄·7H₂O, and also form the double salts with the alkali sulphates MeSO₄·7H₂O, while Ti, Va, Cr, Mn, Fe, Co, Rh, and Sr in the trivalent state form isomorphous alums with the general formula Me^{III} (SO₄)₂R·12H₂O.

Those elements which occupy a position nearer potassium, viz. Ca, Sc, Sr, Y, no longer possess this property, but rather yield salts which closely resemble those of potassium, sodium, and lithium. A series of such similarities can be mentioned. Again, since the maximum valency of the intermediate elements shows, with increasing atomic weight, a periodic change similar to that of the elements of the previous series, so, in like manner, an agreement is to be found in the composition of those compounds which exhibit the maximum valency. The isomorphism referred to above constitutes one example, others are the agreement in composition between the chromates and sulphates, the permanganates and perchlorates, etc. Those fifteen elements inserted in the caesium series must occupy a position with reference to the previous series, intermediate between barium and the homologue of yttrium. This position is assigned to them on account of their chemical properties.

That the rare alkaline earths should exhibit such extraordinary similarities in their chemical properties will appear quite natural when it is remembered that both Sr and Y closely resemble one another. The limits between which variation is possible are so narrow that the formation of elements which differ sharply from one another is no longer possible, and we therefore find that all the rare earth metals possess the characteristics of more or less positive trivalent alkaline earths. But these metals do not correspond to those of the aluminium group. This is specially noticeable in their inability to form alums and in their much stronger electropositive character. The latter property makes itself evident in the neutrality of the aqueous solutions of the salts of lanthanum, terbium, and dysprosium.

Finally, when we assume, as Mendelejeff¹ has done, that a metalloid element is wanting in the hydrogen series, its analogy is found in the five elements intermediate between Li and F, or Na and Cl. The five elements form a complete transition series between the strongly positive and the strongly negative elements, for they are intermediate not only in position but also in their chemical and physical properties.

The result of the foregoing analysis may be summed up in the following words:—

The periodic system consists of series of elements which exhibit a periodic relationship, not only in the number which makes up the series, but also in the properties of the additional elements. This relationship will find an even simpler expression in the results of future research on the elements.

II. The Chemical Compounds.

A. General Part.—The Doctrine of Valency.

Our ideas of valency owe their origin to the attempts made to obtain a numerical expression for those intramolecular affinities which, from the consideration of chemical reactions, are assumed to be the cause of the integrity of the molecule. The fundamental graphical ideas of valency consequently are constitutional and structural formulæ. In such formulæ the intramolecular attractions are represented by lines between the atoms under consideration. The number of lines in each case represents the number of elementary atoms with which an atom can enter into chemical union, and therefore represents the binding value of the latter. This binding value is termed the valency of the atom, and we therefore have in the doctrine of valency a complete picture, according to definite rules, of the theoretical connotations of structural formulæ.

I. The Evolution of the Doctrine of Valency.

An analysis of the evolution of structural formulæ teaches that the alterations which they have undergone from time to time have

On reading Walden's obituary notice on Mendelejeff (Chem. Zeit., 1907), the author became aware for the first time that Mendelejeff had predicted that a new element of halogen group would be found with the atomic weight of three.

always aimed at their spacial configuration. Moreover, such formulæ have continually developed towards nucleus formation, in that one definite atom became the central atom. As a result the number of valencies, on this central atom, were gradually increased. A direct outcome of this progressive development in structural formulæ was the increase in the numerical valency value attaching to an atom.

To illustrate the facts the phases in the development of structural formulæ and of the doctrine of valency are briefly reviewed in the following paragraphs.

1. The Development of Structural Formulæ.

In their original formulation the atoms of chemical compounds were assigned an equal value (Gay Lussac). The first change came with the introduction of the conception of polybasic acids and polyacidic bases. It had long been known that certain bases possessed the property of being able to saturate more than one molecule of acid. This observation had received little notice until Williamson, in 1851, redirected attention to it by formulating such polyacidic bases as condensed water types. He supplemented this idea by pointing out that polybasic acids also existed, in which the hydrogen atoms could be replaced either by basic or acidic residues. On working out these substitution processes more fully it was recognized that certain elementary atoms could form basic or acidic oxygen compounds, of the condensed water type, containing several replaceable hydrogen atoms. Hence, in the extended theory of condensed water types, we have for the first time in the history of chemistry the possibility of classifying chemical compounds on the basis of structural formulæ. As an example of the change thus brought about in the formulation of chemical compounds, the case of ferric-hydroxide may be quoted. Formerly Formula I. represented this compound; now, as in Formula II., the iron atom is the central atom-



The next step in this development came with the "nucleus-formulæ" of sulphuric acid, perchloric acid, etc. As a result of this



new method of writing formulæ, numbers of structural formulæ which earlier were written as chains were transformed into "central" formulæ. The great change thus brought about in the graphic representation of many compounds can be best appreciated by placing these different formulæ side by side—

This metamorphosis from the chain to the nucleus formulæ was only recently placed upon a firm basis. By means of the new methods for the determination of molecular weights, it was shown that salts in which the metallic nucleus exhibited different valencies contain only one such nucleus, and this was proved to be true irrespective of the degree of unsaturation of the metallic atom. When this has been demonstrated the last residue of the chain formulæ, which had survived from the time of constant valency, was laid aside and no longer applied to simple inorganic compounds. By taking ferrous chloride as an example, this change can be represented thus:

$$\frac{\text{Cl}}{\text{Cl}} = \frac{\text{Cl}}{\text{Cl}} = \frac{\text{Cl}}{\text{Cl}} + \text{Fe} < \frac{\text{Cl}}{\text{Cl}}$$

However, large classes of compounds which at that time it appeared impossible to represent by central formulæ remained untouched, while simpler formulæ were being assigned to the other compounds. An attempt to prepare such formulæ would then have been quite useless, because the experimental material was still incomplete and the necessary collection of facts was wanting. The classes of compounds referred to are the metal ammonium salts, the hydrates, and the double salts. The properties of these compounds are developed in the following pages.

Independently of one another, Blomstrand, for the metal ammonium salts and the double salts, and Würtz, for the hydrates, developed formulæ which present a striking resemblance to the

¹ Chemie der Jetztzeit. Heidelberg, 1869.

² La Théorie Atomique. Paris, 1879.

chain formulæ of sulphuric and perchloric acids; for, strange to say, it was Bloomstrand who, by his penetrating and expert criticism, showed the chain formulæ of sulphuric acid to be untenable.

The following examples will serve to illustrate these formulæ:-

Compare with these formulæ the corresponding ones of potassium sulphate and potassium platinochloride—

$$K-O-O-S-O-O-K$$
; $K-Cl=Cl-Pt-Cl=Cl-K$

The consideration of these formulæ shows that the theoretical treatment of "molecular compounds" had reached the same stage as "valency compounds" reached before the statement of the conception of variable valency.

A light is therefore thrown upon the evolution of our conceptions of the construction of the molecule, by showing that the accurate investigation of these molecular compounds has followed an exactly similar process of reformation in structural formulæ, as had already taken place in the chain formulæ of valency compounds.

In place of the chain formulæ, which were inadequate to explain the newly discovered properties of molecular compounds, others have been proposed which assigned a central position to the metal atom. These central formulæ give better expression to the stability and properties of the molecular compounds than the older formulæ admitted of. The rearrangement in graphic representation which such molecular compounds have undergone will be clear on comparing the following examples:—

$$\begin{array}{c} \text{Cl-NH}_{3}\text{--NH}_{3}\text{--NH}_{3}\text{--Co--NH}_{3}\text{--NH}_{3}\text{--NH}_{3}\text{--Cl} \\ \text{Cl} \\ \text{Cl} \\ \text{Co--NH}_{3}\text{--NH}_{3}\text{--NH}_{3}\text{--NH}_{3}\text{--Cl} \\ \text{Chain formulæ.} \\ \\ \begin{bmatrix} \text{NH}_{3} \\ \text{NH}_{3} \\ \text{NH}_{3} \\ \end{bmatrix} \text{Co} \\ \begin{pmatrix} \text{NH}_{3} \\ \text{NH}_{3} \\ \text{NH}_{3} \\ \end{bmatrix} \text{Cl}_{2} \\ \\ \text{Nucleus formulæ.} \\ \\ \text{Nucleus formulæ.} \\ \\ \\ \end{bmatrix} \text{Cl}$$

The analogy between these rearrangements, widely separated in point of time, but important to the uniformity of structural formulæ,

becomes clearer by placing in their proximity the analogous formulæ:—

$$K-O-O-S-O-O-K \rightarrow 0 S CK$$

$$K-Cl=Cl-Pt-Cl=Cl-K \rightarrow Cl Pt ClK$$

2. The History of the Conception of the Valency of the Elementary Atom.

As already mentioned, every remodelling of structural formulæ led to a further development of the conception of valency. This conception was introduced in the science by the theoretical application of Williamson's principle (1853) of referring compounds to condensed types and the relationship between this and the original conception of copulated compounds (gepaarten verbindungen) developed by Frankland (1853) as a result of his researches on the organo-metallic compounds. Odling was the first to assign valency marks to the atom.

Valency is a property of the atom by which the latter is enabled to attract and bind to itself a definite invariable number of other elementary atoms. In this fashion Kekulé conceived valency to act, and consequently expressed his ideas in the following words: I "The theory of atomicity is a modification of Dalton's theory. It is formulated to explain a point where the latter's theory fails, viz. why the atoms of the different elements prefer to combine in certain proportions rather than in others. Atomicity is therefore a fundamental property of the atom, which is just as constant and invariable as atomic weight. To assume that this atomicity is variable, that one and the same body can function at one time with one and at another with a different atomicity would, however, be to use the word in a sense entirely different from that which I gave to it, when I suggested it." This conception of Kekulé leads to the idea that the number of units of valency on an atom is invariable. In its essentials this was the teachings of constant valency, an idea which chemists to-day admit to be inaccurate.

For reasons which will be discussed subsequently, the simple conception of Kekulé was relinquished, and in its place valency

was understood to be a numerical conception, the value of which depended upon the nature of the atoms combining with one another. Thus the idea of valency lost its original simplicity, and this became increasingly justified as further research showed the manifold variations which the elements exhibit in their compounds. The chief value of valency, viz. the yielding of a trustworthy foundation for the construction of constitutional formulæ, was consequently lost. Moreover, it soon became evident that the current ideas of valency, which had proved so extraordinarily fruitful in organic chemistry, were unable to yield satisfactory structural formulæ for large groups of inorganic compounds. As a result of many such attempts it may be taken as conclusively proved that the doctrine of valency, although adequate to provide constitutional formulæ for carbon compounds, is unable to do so for other elements. Consequently the theory of the forces which are responsible for the building up of inorganic molecules had to be developed independent of the original conception of valency, i.e. solely from the properties of the compounds in question.

When the new laws governing structural formulæ were transferred and applied to elements other than those through which they were developed, it was seen that they were applicable to most elementary atoms, for the latter were found to be able to yield compounds, the existence of which could not be predicted from the earlier conceptions of valency and hence could not be deduced from them.

The new ideas, thus obtained, on the combining capacities (Bindevermögen) of the elementary atoms is called the "doctrine of co-ordination" (Koordinationslehre). A theoretical connection must exist between the doctrine of valency and that of co-ordination, which will combine both to a general theory of valency. Such a connection can be proved in many isolated instances, but a complete and satisfactory unification of these theories into one harmonious whole has yet to be formed. Such a general theory must admit not only of the deduction of valency structural formulæ, but also of co-ordination formulæ, and therefore the most important and pressing problem of valency resolves itself into the discovery and formulation of the general law which expresses all the combining possibilities of the atom.

II. On the Number of Valencies.

- 1. The Number of Principal Valencies.
- (a) Introductory considerations concerning the Conception of Principal Valencies.

When the molecular composition of compounds of the first order, e.g. those of hydrogen:

are examined, it is seen that the number of hydrogen atoms in combination with one atom of another element is different in each case. It must further be concluded from the chemical behaviour of these compounds that the hydrogen atom retains its connection with the other atom of the molecule through an exchange of affinity between the two atoms, hence the following constitutional formulæ are assigned to these compounds:—

$$\mathbf{H} - \mathbf{I} \qquad \mathbf{H} \qquad$$

It follows, therefore, that the combining values of the different elements for hydrogen is variable. This combining value of an element is termed its valency. Since hydrogen in these simple compounds combines with only one elementary atom, it is said to be monovalent, and atoms are said to be mono-, di-, tri-, and tetravalent according to the number of hydrogen atoms with which they unite.

The valency of the elements can be deduced from the composition and constitution of other compounds, e.g. those of the halogens, by processes analogous to those used with hydrogen compounds. In this way we obtain the valency of F, Cl, Br, etc. Since these elements are monovalent towards hydrogen, it was originally believed that the elements would exhibit the same valency towards chlorine as towards hydrogen. Some elements, e.g. carbon, have justified this expectation; moreover, the valency of some polyvalent elements (oxygen, sulphur, and nitrogen) as deduced from their hydrogen and carbon compounds is identical, for carbon combines with four hydrogen atoms, or two divalent oxygen atoms, or one divalent nitrogen and a monovalent atom, etc. If its capacity for

THE CHEMICAL COMPOUNDS

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combining with hydrogen is taken as the standard, carbon has, therefore, a constant valency equal to four units; and, moreover, in this respect carbon displays a very simple behaviour, inasmuch as only one valency is ever active in reference to a particular element. To be sure, carbon forms with oxygen not only carbon dioxide but also carbon monoxide. But considering the thousands of carbon compounds this is a very rare exception indeed, and in comparison with the otherwise normal behaviour of carbon scarcely merits consideration, especially when it is possible, by making certain assumptions, to explain this abnormal behaviour.

The valency of carbon in its compounds is so constant, that the doctrine of constant valency is the logical outcome of their study, particularly as this conception has proved itself to be of such extraordinary value for their investigation. But when the conceptions of valency thus developed were applied to the compounds of other elements it became evident that the doctrine of constant valency was untenable, for their valency was found to be variable. The results of these researches are discussed in the following pages.

(b) On the Variability of the Principal Valencies.

(a) Proof of the Variability of the Principal Valencies.

That the valency of the elements is not constant but variable is the conclusion drawn from a comparative study of the composition and constitution of different classes of compounds composed of different elements. The manner in which this variable valency makes itself evident will be made clear in the following paragraphs.

1. The Atoms of Certain Elements exhibit Different Capacities for Saturation.

This statement is founded upon phenomena of the following description: An iron atom can combine to form a molecule with either two or three chlorine atoms, an atom of tin with two or four chlorine atoms, and an atom of indium may form molecules with one, two, or three atoms of chlorine, etc. For a long time these phenomena were explained by the supposition that in the lower compounds the apparently unsaturated valencies mutually satisfied each other. In this manner these exceptions were brought into agreement with the doctrine of constant valency, and the following

structural formulæ, which strongly recall chain formulæ, were assigned to them—

These formulæ are incorrect, for it has recently been shown from determinations of the molecular weight of a great number of inorganic chlorides that the molecule contains only one metal atom. This result has been obtained from observations based upon cryoscopic and ebulioscopic determinations. Consequently it appears to have been proved that an elementary atom, according to the conditions, can combine with different numbers of other elementary atoms, without the co-called "free valencies" mutually satisfying each other.

But if this is true, then it is incorrect to speak of the constant valency of the elements, and to select an indefinite combining ratio, e.g. the highest, and refer to it as standard.

Such a proceeding would be very arbitrary, for the facts offer no justification for choosing out a particular valency value (Valenz-zustand) in preference to any other and using it in this manner. When it is desired to describe the valency of an element, it is not sufficient to confine the description to the maximum value, but the different saturation capacities (Wertigkeitsstufen) must also be given; thus: iron is di- and tri-valent, tin is di- and tetra-valent, indium is mono-, di- and trivalent, etc.

2. Certain Elements possess Saturation Capacities which depend upon the Nature of those Elements with which they are in Combination.

The different saturation capacities of the elements, as discussed in the foregoing paragraph, are not yet exhaustively described. For on comparing the valency value of an element in its compounds with other elements, it is seen that the valency value is not invariably a maximum. For example, nitrogen has saturation capacities for oxygen which differ from those for the halogens, and many elements exhibit much higher valency values towards oxygen and fluorine than chlorine and bromine, etc. Accordingly the uniform value laid down by the doctrine of valency is not in evidence amongst these different valencies of an elementary atom; to such an extent is this true that it is doubtful whether there exists a uniform standard for valency. This is the reason for the

vagueness of the conceptions of valency at the present day. For, when the monovalency of the halogens, the divalency of the oxygen group, and the trivalency of the nitrogen group, etc., had been established for their hydrogen compounds, and when the equal valency of the halogens and hydrogens had been used to determine the valency of the metals from their halogen compounds, it was expected that an element, whose valency had thus been fixed, would exhibit the same saturation capacity for another similar element. But this was not confirmed, as may be seen from the following examples: sulphur is hexavalent towards fluorine, but tetravalent towards chlorine; manganese gives an oxide, Mn2O2, in which manganese is heptavalent, while in its highest chloride, MnCl4, it is tetravalent; iron in ferric acid is hexavalent, but in its highest chloride it is trivalent, etc. It is, therefore, impossible to speak of even approximate agreement in the different valency values of an element, so that with regard to its ability to combine with other elements it is likewise impossible to refer to a constant valency value, Such a supposition would postulate in most compounds such a large number of unsaturated valencies, that we would seek in vain for a satisfactory formula. In ferrous chloride, for example, we would have to suppose that there were four unsaturated valencies, in manganous chloride five, and in sulphur chloride two. It, therefore, appears more natural to ascribe to the element that valency which observation gives it, than a capacity for saturation with another similar molecule the value of which is dependent upon the nature of the combining atoms. Consequently, when speaking of the valency of an element, it is essential to mention with what other element that value takes effect, e.g. iron is di- and tri- valent towards chlorine, but is tetravalent towards sulphur and hexavalent towards oxygen, etc.

3. The Valency of an Element may depend upon External Conditions.1

It is well known that the general affinity ratios of the elements are dependent upon external conditions, particularly on the temperature. It is consequently to be expected that the valency of the elements would be likewise a function of these external conditions, e.g. of the temperature. That this is justified is the person in the phenomena of dissociation with rise of temperature, viz. CO₂

¹ Cf. Billitzer, Wiener Monatshefte, 25, 745 (1904); and also Abegg and Hinrichsen, Zeitsch. anorg. Chem., 48, 122 (1905).

dissociates into CO + O and SO_3 into SO_2 and O, etc. Further, to this category belongs the decomposition at high temperatures of saturated into unsaturated hydrocarbons. From these examples the general law may be formulated, that valency decreases with rising temperature. That pressure likewise plays an important $r\hat{o}le$ is obvious, for at the temperature of the experiment the existence of a dissociable compound is determined by the pressure exerted by the products of dissociation.

Consequently we arrive at the conclusion that valency is a function of the temperature and pressure. It is also possible that other physical factors may exert a controlling influence on valency; for example, it is not improbable that certain classes of compounds can exist only in solution, but not in the solid state, or vice versa. Up to the present the influence on valency of such physical factors has received little attention, and it would not be without interest in simple cases to study, for example, how the maximum valency of an element varies with the temperature.

β. On the Possible Numerical Value of the Principal Valencies.

Having established that valency is a function of various factors, the numerical value of which fluctuates within wide limits and finds expression in the composition of chemical compounds, it seems appropriate to inquire how and within what limits this numerical value varies. The answer is that probably every element can exhibit every intermediate value up to its maximum valency.

In support of this statement there exists already a large number of elements which possess a complete valency series, which the following examples serve to illustrate:

Manganese: MnCl₄, MnCl₃, MnCl₂;

Molybdenum: MoCl₅, MoCl₄, MoCl₃, MoCl₂;

Vanadium: VCl₅, VCl₄, VCl₃, VCl₂;

Manganese: MnO, Mn₂O₃, Mn₃O₄ MnO₂, MnO₃, Mn₂O₇

Once more it must be stated emphatically that it is inadmissible to double the formulæ of those compounds whose valency is below the maximum value, except the experimental facts sanction it. The author himself has shown that a great number of such compounds possess the simple formula, and these results have been confirmed by other investigators.

The compounds of some metallic sesquioxides, with acetylacetone, which were always written double, the two metal atoms being

bound one to another, have been shown to be correctly represented by the single formula. Urbain and Debierne determined the molecular weights of the acetylacetonates of iron, manganese, cobalt, chromium, and aluminium in benzene solution, and arrived at this conclusion.

It is remarkable that the maximum valency of electro-negative elements is attained in compounds formed with other negative elements, e.g. the halogens with oxygen, Cl_2O_7 ; sulphur with oxygen, SO_3 ; and with fluorine SFl_6 , etc., while electro-positive elements exhibit their highest valency with other electro-positive elements, e.g. the alkali metals in amalgams NaHg_6 , KHg_{12} , etc.

The maximum valency is also dependent upon the positions of the element in the periodic system, and this peculiarity is especially evident in the hydrogen and oxygen compounds. For, as is well known, there is a regular rise and fall in the valency of the hydrogen compounds in the short periods, while, on the other hand, there is a regular increase in the valency of the oxygen compounds to the maximum value of seven.

An exhaustive examination of the dependence of valency on position in the periodic system would take up too much space and lead to nothing new. So we will consequently dismiss it, and the interesting communication of Abegg's,² in which he supposes all the elements to have a constant maximum valency of eight, can receive only passing mention.

δ. Conclusions.

The phenomena discussed in the previous paragraphs can be reduced to the following conclusions.

Valency is a numerical conception, the value of which expresses the combining ratios of the elements. It is not an inherent property of the atom as such, but is dependent upon the nature of the atoms with which it enters into combination and also upon the external physical conditions. The valency of an element can therefore exhibit different values towards another element, i.e. valency is a variable property. Such, then, is the doctrine of variable valency.

¹ Compt. rend., 129, 302 (1899).

Abegg, "Versuch einer Theorie der Valenz und der Molekularverbindungen," Christiania, 1902; and Abegg, "Die Valenz und das periodische System. Versuch einer Theorie der Molekularverbindungen," Zeitsch. anorg. Chem., 39, 381 (1904).

2. The Number of Auxiliary Valencies.

(a) Introductory Considerations on Compounds of Higher Order.

Up to the present the application of the theory of valency to binary compounds has been considered. To this class belong Compounds of the First Order, i.e. the simple compounds of hydrogen, the halides, the oxides, etc. But there exists a more complicated class, the members of which are formed by the union of binary compounds. This process may be represented by the general equation:

$$AB + CD = \begin{pmatrix} C \\ A \\ D \end{pmatrix}$$

Now, since AB and CD represent simple compounds, the product resulting from their combination may be called either a molecular or a complex compound. But many compounds formed in this way have had, in terms of the doctrine of valency, a satisfactory structural formula ascribed to them. Consequently they can no longer be considered as molecular compounds, and seeing that the conception of "complex compounds" has already a definite electrochemical meaning, it therefore appears desirable to reintroduce the term "Compounds of Higher Order"; a term first used by Berzelius for such compounds. The use of this term has the additional advantage of excluding any possibility of misconception, for it includes all such compounds as those mentioned above.

Compounds of higher order can be divided into sub-groups according to the classes of molecules which take part in their formation. In this way, if one component is ammonia, ammonium addition products are obtained, of which the most important subclass is the metallic ammino-compounds. These compounds are formed by the union of ammonia and metallic salts. If water is added to compounds of the first order, hydrates are obtained, to which class the oxygen acids belong. When simple halides combine together to form compounds of higher order, double halides result, which form a group of the so-called double salts, etc. In the special part of this book examples are given of many such combinations, and it will then be seen how extraordinarily varied are the types of compounds to be expected.

In the formation of compounds of the higher order from those of

the first order, the principal part is played by affinities which differ from the ordinary valencies. The object of the following discussion is to demonstrate this and also to characterise these new affinities (affinitäteskräfte). Since, however, the examination of the compounds of higher order has shown that they may be sharply divided into two groups, i.e. addition- and substitution-compounds, it is intended first to consider the addition-compounds and later the remaining class.

(b) On the Constitution of Addition Compounds.

a. Introductory Considerations.

Almost all compounds of the first order (saturated hydrocarbons form the sole exception) possess the property of combining with other compounds of like nature. The truth of this may be illustrated by a simple example, which will at the same time serve to exemplify how diverse such addition products may be. Sulphur trioxide gives the following addition products:

$$O_3S + OH_2 = O_3S \cdot OH_2^{-1}$$

 $O_3S + ClH = O_3S \cdot ClH$
 $O_3S + NH_3 = O_3S \cdot NH_3$

¹ These formulæ are not intended to be structural formulæ, but only to draw attention to the combining units.

The chemical examination of such compounds shows that the combination of the heterogenous molecules takes place through the combination of the more positive atom of sulphur trioxide, *i.e.* sulphur, with the negative elements of the other molecules, *i.e.* oxygen, chlorine, and nitrogen, in the way schematically represented in the following equations:

$$0 = \frac{0}{8} + OH_{2} = O = \frac{0}{8} ... OH_{2}$$

$$0 = \frac{0}{0} + OH_{2} = O = \frac{0}{8} ... OH_{2}$$

$$0 = \frac{0}{0} + CIH = O = \frac{0}{8} ... CIH$$

$$0 = \frac{0}{0} + OH_{2} = O = \frac{0}{8} ... CIH$$

$$0 = S + NH_3 = 0 = S ... NH_3$$

$$0 = S + NH_3 = 0 = NH_3$$

- B. On the Cause of the Formation of Addition Compounds.
- 1. Old Explanation and Proof that it is Untenable.
 - (a) Development of the Theory.

As is well known, the doctrine of valency explains the formation of oxygen acids and their salts by assuming that the doubly bound oxygen atoms can be transformed into or be replaced by hydroxyl groups; thus, for example, the formation of sulphuric acid may be expressed by the scheme:

$$\int_{0}^{0} \int_{S=0}^{H} = \int_{0}^{0} \int_{S=0}^{OH} \int_{OH}^{OH}$$

or the formation of chlorsulphonic acid by the scheme:

$$\int_{0}^{\infty} \int_{S=0}^{\infty} + ClH = \int_{0}^{\infty} S \left(\int_{OH}^{Cl} \right)$$

To this apparently simple and satisfactory explanation of such addition processes is to be ascribed the fact that the theory of the constitution of inorganic compounds has remained in its initial state. That such constitutional formulæ, as deduced from the doctrine of valency, are incorrect will be shown in the following paragraphs.

(b) General Objections to such Valency Formulæ.

1. Since the explanation depends upon the divalency of oxygen, all compounds of divalent metalloids, i.e. oxides, sulphides, etc., have a special place allotted to them, for it is impossible for compounds of monovalent elements, e.g. the halides, to form groups similar to hydroxyl. Consequently such formulæ prevent discussion on the possibility of analogous formulæ being given to compounds formed by the combination of fluorides, chlorides, bromides, iodides, etc., i.e. double halides. An analogy between the combination of two oxides:

$$K_2O + SO_3 = K_2SO_4$$

and the combination of two chlorides:

$$KCl + AuCl_3 = K(AuCl_4)$$

is according to this theoretical conception not only not to be expected, but also is not possible. Sufficient proof of this is to be found in the many fruitless attempts which have been made to bring the halogen double salts within the valency system.

But such an analogy really exists. The halogen double salts therefore belong to those compounds whose constitution can only be represented by straining the customary ideas on valency, and for a long time have been pushed on one side as unimportant molecular compounds. Several large classes of compounds have suffered the same fate.

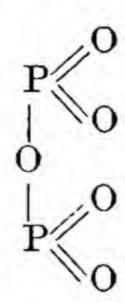
2. Since the explanation of addition reactions, deduced from the doctrine of valency, requires the radicle, hydrogen, metal, etc., which is taken up by the doubly bound oxygen to be very mobile, it follows that a similar explanation cannot be advanced to explain the constitution of those addition compounds in which such mobility is impossible. The ether addition products afford examples of this latter class of compounds.

(c) Special Objections to such Valency Formulæ.

As well as these general objections to the idea that the formation of hydroxyl groups is the cause of the combination of oxides with other compounds, there exist several special reasons. Such are to be found in the behaviour of oxides on hydration. According to the doctrine of valency, those oxides richest in oxygen, RuO₄ and OsO₄, should prove the most susceptible to the formation of hydrates. As a matter of fact, in spite of four doubly bound oxygen atoms, these oxides are unable to take up water; in other words, they do not act as acidic anhydrides.

In general it can be shown that the number of water molecules which are taken up by an oxide are independent of the number of doubly bound oxygen atoms, whereas, according to the doctrine of valency, it is the number of doubly bound oxygen atoms which determine the number of molecules which are taken up. Chlorine heptoxide:

although containing six doubly bound oxygen atoms, only takes up one molecule of water, while phosphorus pentoxide



which contains only four doubly bound oxygen atoms, takes up three molecules of water, etc.

Since doubly bound oxygen is still present in the hydrated forms HClO₄, H₂SO₄, H₃PO₄, and if these forms were produced by the addition of water, then it would be difficult to understand why perchloric acid does not also act as heptabasic, H₇ClO₇, and phosphoric acid as pentabasic, H₅PO₅.

On the other hand, if without any preconceived opinion we consider the composition of the oxygen acids $H(ClO_4)$, $H_2(SO_4)$, $H_3(PO_4)$, etc., it becomes clear that the number four appears to be the limiting number of the oxygen atoms in these acids. For it is not only independent of the number of hydroxyl groups present, but also of the number of doubly bound oxygen atoms, and perhaps this may be the reason why the oxides RuO_4 and OsO_4 are unable to form hydroxyl. The hydroxylation of doubly bound oxygen cannot therefore be considered as the cause of the formation of addition products with oxides, and when it occurs is consequently only to be considered as a secondary phenomenon.

Another objection to the deductions made from the doctrine of valency as to the cause of the formation of addition products, is to be found in the fact that water not only combines with oxides, but also with chlorides, iodides and many other classes of compounds.

Some authors endeavour to prove the existence of a difference between the formation of hydrates by oxides and by other compounds, e.g. chlorides, fluorides, etc., by supposing that in the former case oxyhydrates are produced, while in the latter this is impossible. But the properties of the compounds in question do not justify such a difference.

The hydrates of the halogens in many cases behave in exactly the same way as those of the oxides. In order to demonstrate this, compare the behaviour of sulphur trioxide and gold chloride with water. Both compounds combine with one molecule of water according to the following equation:

Both the product formed by the combination of sulphur trioxide with water and that resulting from the combination of gold chloride and water are acids. Yet according to the doctrine of valency, in the latter case, the formation of hydroxyl is impossible, nevertheless a compound with acid functions is produced. A difference is neither to be found in the method of preparation, nor in the behaviour of the resulting hydrate, and hence it is very arbitrary to make such a difference.

It is very probable, though not as yet definitely proved, that it is the oxygen atom of the water that is in combination with the gold atom. When this has been proved, the analogy between sulphuric acid and the hydrate of gold choride will be complete. As will be shown in what follows, it is possible, in the case of the hydrates of other chlorides, to prove their constitution completely.

- 2. Explanation of the Formation of Addition Compounds by means of Co-ordination Formulæ.
- (a) On the Addition Compounds of Platinum Chloride and their Constitutional Formulæ as deduced from the Doctrine of Valency.

It has been shown that the theory of principal valencies cannot explain the formation of oxygen acids, and in like manner it can be shown that it is incapable of explaining the formation of all possible compounds of higher order.

Although the constitutional formulæ of the oxygen compounds, as deduced from the doctrine of valency, expresses the behaviour of these compounds, it does not do so when double halogens, metal ammonium compounds, etc., are considered; the formulæ of these compounds when similarly deduced is in contradiction to their chemical behaviour. The following facts make this evident. Platinum chloride behaves similarly to sulphur trioxide in its tendency to form addition products with certain binary compounds.

It combines, for example, with hydrochloric acid to form the dibasic chloro-platinic acid:

$$Cl_4Pt + 2ClH = Cl_4Pt(ClH)_2$$

and with two molecules of water to form a hydrate:

$$Cl_4Pt + 2OH_2 = Cl_4Pt(OH_2)_2$$

and also with one molecule of water and one molecule of hydro chloric acid:

$$Cl_4Pt + OH_2 + ClH = Cl_4Pt : OH_2 \\ ClH$$

Both Cl₄Pt(OH₂)₂ and Cl₄Pt OH₂ are dibasic acids.

Platinum chloride forms an addition compound with ammonia:

$$Cl_4Pt + 2NH_3 = Cl_4Pt(NH_3)_2$$

in which none of the four chlorine atoms have ionogene properties, and when it at the same time takes up both ammonia and chloride the resulting compound:

$$Cl_4Pt + NH_3 + .ClR = Cl_4Pt \cdot \frac{NH_3}{ClR}$$

behaves as the ammonium salt of a complex acid

$$\left(\operatorname{Pt}^{\operatorname{Cl}_5}_{\operatorname{NH}_3}\right)\operatorname{H}$$

The analogy between the addition compounds of sulphur trioxide and platinum chloride is complete, and since the constitutional formulæ of (SO₃. OH₂), (SO₃. ClH) and (SO₃. NH₃) correspond, it follows that the constitutional formulæ of (PtCl₄(ClH)₂), (PtCl₄(OH₂)₂), (PtCl₄(OH₂)(ClH)), (PtCl₄(NH₃)₂), and (PtCl₄(NH₃) (ClR)) must be similar. But the formulæ which have in reality been proposed are the following:—

The formula for chloroplatinic acid with trivalent chlorine first proposed by C. W. Blomstrand is still advocated to-day—

For the two isomeric metallic ammonium compounds: Cl₄Pt(NH₃)₂, the formulæ

were proposed by P. T. Cleve and S. M. Jörgensen. They contain pentavalent nitrogen, and assume that pentavalent nitrogen atoms can form a chain.

The compound Cl₄Pt NH₃ had the formula

$$\begin{array}{c|c} & & \text{Cl} & \text{Cl--Cl--R} \\ & & \text{Cl} & \text{NH}_3\text{--Cl} \end{array}$$

ascribed to it.1

Up to the present no formula has been proposed for the hydrate of platinum chloride, $Cl_4Pt(OH_2)_2$; but since it corresponds to the dibasic acid, chloroplatinic acid, it ought to have the formula:

containing trivalent chlorine and tetravalent oxygen. On the other hand, since it is a compound formed by the addition of water to platinic chloride, it corresponds to the ammonium addition compound, and ought, from this standpoint, to have the formula:

containing two tetravalent oxygen atoms, and since neither of these formulæ expresses its relation to platinic acid, Pt(OH)₄. 2H₂O, we are compelled, since this relationship must be expressed, to give it a third formula, etc. Hence it is evident that many formulæ can be proposed from considerations of valency and the isolated properties of the component elements, but none of these formulæ admit of the harmonious correlation of the characteristic properties of the compound. Moreover, these formulæ are unable to give expression, by means of similarly constituted formulæ, to the analogy existing between the modes of their formation. This

¹ S. M. Jörgensen, Zeitsch. anorg. Chem., 24, 158 (1900).

analogy is at least quite as definite as that existing between the addition compounds of sulphur trioxide. We therefore arrive at the conclusion that the doctrine of valency is unable to yield satisfactory pictures of the formation and constitution of these compounds, and we are therefore compelled to deduce their constitutions directly from their properties and without any reference to the customary ideas on valency.

(b) Constitution of the Ammonium Compounds.

The platinum ammonium compounds, Pt $\frac{\text{Cl}_4}{(\text{NH}_3)_2}$, exist in two isomeric forms, i.e. platiniammin and platinisemidiammin chloride. The cause of this isomerism, which is steric in nature, will be considered in a later chapter. At present we are only concerned with the constitution of these isomers. Measurement of their electrical conductivity shows that in dilute aqueous solution they are so little dissociated that hardly any chloridion is present. This behaviour is easily understood when it is assumed that each chlorine atom is linked directly to the platinum atom. For were the chlorine atoms linked to nitrogen, as in ammonium salts, we would expect the aqueous solutions of these platinum salts to be strongly electrolytically dissociated. Such dissociation could be proved by the great conductivity of the solution, the development of hydrochloric acid on treatment in the cold with sulphuric acid, and by the precipitation of silver chloride from the aqueous solution. But since these reactions fail to prove the presence of chloridion, the conclusion that the chlorine atoms are bound directly to the platinum atom is unavoidable.

The position of the ammonia in the molecule also must be determined, and in this connection the following three formulæ require consideration:

Cl
$$Pt$$
Cl NH_3 Cl NH_3)Cl Cl NH_3
Cl NH_3)Cl Cl NH_3
Cl NH_3)Cl Cl NH_3
Cl NH_3
Cl NH_3)Cl Cl NH_3

That the first formula is unsatisfactory is shown by the possibility of removing the chlorine atoms from the molecule without at the same time disturbing the ammonia molecules. For

example, two chlorine atoms may be removed by reduction, thus producing a compound, with the formula $Cl_2Pt(NH_3)_2$, in which both chlorine atoms are again non-dissociable. Further, it is possible by double decomposition with silver and other metallic salts to prepare a series of compounds, $X_2Pt(NH_3)_2$, from the compound $Cl_2Pt(NH_3)_2$ without in any way interfering with the ammonia. Consequently the chlorine atoms do not act as links between the ammonia and the platinum atoms. Both atoms of ammonia therefore must be directly attached to the platinum atoms; any other possibility is excluded.

That they exist as ammonium salts, as formula II. suggests, has already been shown to be impossible, since all four chlorine atoms behave similarly and are in direct connection with the platinum atom.

Further, the existence of compounds of the general formula Cl_4Pt : $|ClR| NH_3$, in which an ammonia molecule and a molecule, ClR are bound to the platinum atom, afford satisfactory proof that both ammonia molecules in $Cl_4Pt(NH_3)_2$ are separately bound to platinum. Formula III. also gives expression to the possibility of Cl_4Pt : NH_3 passing by the action of ammonia into $Cl_4Pt(NH_3)_2$. This change, which may be represented by the equation—

$$Cl_4Pt_{ClR}^{NH_3} + NH_3 = Cl_4Pt_{NH_3}^{NH_3} + ClR$$

shows that a molecule of ammonia replaces ClR in the compound $\text{Cl}_4\text{Pt}\frac{\mathrm{NH}_3}{\mathrm{ClR}}$.

The compound Cl_4Pt : $\frac{NH_3}{ClR}$ admits theoretically of three possible formulæ :

The first formula is inapplicable, because the replacement of CIR by ammonia yields Cl₄Pt(NH₃)₂, and in the latter ammonia cannot be bound to chlorine.

The second formula, which hardly deserves serious consideration, is excluded by the properties of the compound, for if the chlorine atom is bound to ammonia it must appear as chloridion in solution, and this is not supported by experiment. Hence, the third formula, in which ClR and NH₃ are bound directly to the platinum atom, is the only possible one. Consequently, it has also been shown that in the compound Cl₄Pt (NH₃)₂, which is produced directly from Cl₄Pt · NH₃, both ammonia molecules are in direct connection with . ClR

the platinum atom and are independent of each other.

That this connection is maintained by the nitrogen and not by the hydrogen of ammonia, is shown by the possibility of replacing the ammonia by pyridine and other tertiary amines. The structural formula of the compound $\text{Cl}_4\text{Pt}(NH_3)_2$ therefore can only be

(c) The Constitution of Chloroplatinic Acid.

The compound Cl_4Pt : $\overset{\text{NH}_3}{\text{ClR}}$, in which, as has already been shown, NH_3 and ClR are directly bound to platinum, is closely related to chloroplatinic acid and its salts PtCl_6R_2 . These genetic relations may be expressed by the formulæ:

$$Cl_4Pt^{\cdot}_{\cdot NH_3}^{\cdot NH_3}$$
 $Cl_4Pt^{\cdot}_{\cdot ClR}^{\cdot NH_3}$ $Cl_4Pt^{\cdot}_{\cdot ClR}^{\cdot ClR}$

and the accuracy of these formulæ admits of simple experimental confirmation. Thus, it is possible to prepare from chloroplatinic acid the other types of compounds, e.g. from pyridine chloroplatinate compounds may be prepared which contain one and two molecules of HCl less than the mother compound:

$$Cl_4Pt$$
: $ClHPy$ \rightarrow Cl_4Pt : Py \rightarrow Cl_4Pt : Py

From this it must be concluded that the HCl in chloroplatinic acid is linked directly to the platinum atoms, just like pyridine and ammonia in the compounds Cl₄PtPy₂ and Cl₄Pt(NH₈)₂. The constitutional formula for chloroplatinic acid is therefore

(d) The Constitution of the Hydrate of Platinum Chloride.

When platinum chloride takes up two molecules of water, the compound $\text{Cl}_4\text{Pt}(\text{OH}_2)_{\scriptscriptstyle{\Sigma}}$ is produced. The addition of water has no effect on the chlorine atoms, *i.e.* they do not receive ionogene properties, but remain linked directly to the platinum atom. The water, however, which already is slightly electrolytically dissociated, undergoes by the process of addition an enormous increase in dissociation, so much so that the hydrate acts as dibasic acid:

As a result of this behaviour, silver nitrate does not precipitate chlorine in aqueous solution, but forms a compound of the formula $Cl_4Pt \cdot OH Ag$; other salts of this acid, $(Cl_4Pt(OH)_2)H_2$, can also be prepared. Both platinum bromide and iodide behave in solutions like the chloride. This behaviour shows that the hydrate is completely analogous to the halogen platinic acids.

The following constitutional formulæ for the hydrate are possible:

The last of these formulæ is the only satisfactory one, for the water molecules must be linked directly to the platinum atom as in platinic acid, and in the latter, as is well known, they are linked in this way. The work of Miolati and his pupils has proved this, for

This behaviour of platinum chloride I had already recognized in its complete significance and drawn attention to it in the Vierteljahrsschrift der Naturforschenden Gesellschaft, Zurich, Jahrg., 41, 254 (1896), before the exhaustive work on the hydrates of gold and platinum chlorides of F. Kohlrausch, Wied. Ann., 63, 423 (1897); Hittorf and Salkowsky, Zeitsch. physikal Chem., 28, 546 (1899); Miolati, Zeitsch. anorg. Chem., 22, 445 (1900), had appeared.

he has been able to prepare the following series of compounds which are intermediate between the hydrate of platinum chloride and platinic acid:

$$Cl_4Pt(OH_2)_2$$
 $Cl_3 Pt(OH_2)$ $Cl_2 Pt(OH_2)_2$ $Cl_2 Pt(OH_2)_2$ $Cl_3 Pt(OH_2)_2$ $Cl_3 Pt(OH_2)_2$ $Cl_3 Pt(OH_2)_2$ $Cl_4 Pt(OH_2)_2$ $Cl_5 Pt(OH_2)_2$ $Cl_6 Pt(OH_2)$

This interesting transition series brings out clearly the relationship of platinum chlorhydrate to the hydrate of platinum oxide, $PtO_2 + 4H_2O$ (platinic acid). Any remaining doubt that their constitutions are similar is removed when it is known that the compounds poorer in chlorine are prepared from those richer in chlorine, by replacing chlorine with hydroxyl.

Finally, it is worthy of notice that between platinum chlordihydrate and chloroplatinic acid there exists an intermediate compound, $\operatorname{Cl}_4\operatorname{Pt}: {\operatorname{ClH}}_2$, which still more clearly brings out the close relationship between these compounds, and also offers further confirmation for the constitution of chloroplatinic acid deducted from the platinammines. By introducing these compounds into the above series, we obtain the following summary:

With the exception of the fourth member of the series all these compounds are known; they are all dibasic acids, whose salts completely correspond to the parent acids.

(e) Conclusion.

Our discussion has led us to ascribe the following structural formulæ to the addition compounds of platinum chloride:

These structural formulæ compel the supposition that the platinum atom in platinum chloride possesses the property of being able to unite with two extra groups. Hence, the explanation accounting for such addition reactions, which is offered by the doctrine of valency and which is based upon the polyvalency of oxygen, is superfluous.

γ. The Theoretical Results which follow from the New Constitutional Formulæ for Addition Compunds.

The preceding considerations have shown that the explanation of the formation of compounds of higher order and the deduction of their constitutional formulæ demands a new theoretical basis, which will provide a consistent explanation of the facts. Such a foundation is obtained by making the assumption that the sulphur atom of sulphur trioxide, the platinum atom in platinic chloride, the oxygen in water, the chlorine in hydrochloric acid, and the nitrogen in ammonia, etc., possess a residue of unsaturated affinity, which permits such groups as these to mutually satisfy each other. If the amount of this residual affinity is sufficient to bring about a stable combination between single molecules, then it assumes practically the same rôle as the ordinary valencies, viz. it effects an interdependence between two elementary atoms, and in this way unites two radicles to molecular complex. But these new valencies differ from the ordinary ones because they are unable to unite monovalent radicles (as defined by the doctrine of valency), and therefore it is proposed to call them "auxiliary valencies" (nebenvalenzen) in order to distinguish them from the ordinary or principal valencies (hauptvalenzen).

The formation of compounds of the higher order therefore is brought about by the auxiliary valencies of the compounds of the first order; thus:

But should one of the reacting molecules contain several doubly bound atoms, it is possible for the primary product to pass into a principal-valency compound:

Such a change, however, is not absolutely necessary, for the auxiliary valencies are sufficiently strong to preserve the integrity of the new molecule, if the addition compound, as such, is stable. The change in the type of compound is consequently only a secondary process. The behaviour of the addition compounds of platinum chloride supports this conclusion. For in these compounds, which are formed by the saturation of the auxiliary valencies on the platinum atom, such a transformation is impossible. In all other respects the addition compounds of SO₃ and PtCl₄, completely correspond; thus:

$$O_3S ... OH_2$$
 $O_3S ... ClH$ $O_3S ... NH_3$ $Cl_4Pt ... (OH_2)_2$ $Cl_4Pt ... (ClH)_2$ $Cl_4Pt ... (NH_3)_2$

The addition compounds of platinum chloride consequently differ from those of sulphur trioxide in that they do not admit of their being transformed into the so-called valency formulæ.

It has been found that, like SO, and PtCl, all compounds of the first order possess auxiliary valencies, the saturation of which gives rise to molecular complexes. The clearest proof of the existence of these auxiliary valencies is obtained by experimenting with binary compounds, the acid residue of which is not dissociated electrolytically in aqueous solution.

Under these conditions, and when the acid residue in the addition compound remains undissociated, we are justified in concluding that the added components are bound to the central atom, provided only that it can be shown that they are not bound to the acid residue. The following compounds lend themselves to such experimental proof: PdCl₂, PtCl₂, Co(NO₂)₃, AuCl₃, TlCl₃, etc.

Palladinous chloride combines with two molecules of NH₃, one or two of CO, one of PCl₃, two of tertiary arsine, etc., in the following way:

Platinous chloride takes up two molecules of NH₃, two of tertiary phosphine, one or two of PCl₃, one or two of CO, one of ethylene, etc., thus producing the following compounds:

The properties of all these addition compounds show that both the chlorine atoms of platinous and palladinous chlorides are bound in the same way as in the original compound. This is also true of the chlorine in gold chloride in the compounds:

And the addition of new molecular components must consequently have taken place in the manner indicated by the formulæ. The constitution of the addition compounds in the following cases can with equal clearness be justified.

Cobalt nitrite combines with three molecules of NH3, or one of

NH₃ and one of ethylenediamine, forming triammintrinitrocobalt and amminethylendiamintrinitrocobalt:

$$(NH_3)_3Co(NO_2)_3$$
 and $\stackrel{en}{H_3N}Co(NO_2)_3$

These addition compounds are, within certain limits, monomolecular, and the nitro-group must be in direct combination with the cobalt atom, for the aqueous solution exhibits so small a conductivity that it can be considered a non-conductor.

In like manner thallium chloride takes up three molecules of pyridine, and the properties of the product, which is easily soluble in ether and alcohol, show that it is not a derivative of an ammonium salt. The constitutional formulæ of triammincobaltnitrite, the analogous ethylenediamin compound, and tripyridinthallium-chloride are consequently to be represented thus:

This discussion on the new structural formulæ, for which the term "Co-ordination Formulæ" is proposed in order to distinguish them from the ordinary valency formulæ, leads to the annunciation of a new general principle governing the combining possibilities of the atom: viz. Even when, according to the doctrine of valency, the combining possibilities of an atom are exhausted, it still possesses a particular kind of affinity which enables it to form molecular complexes.

For this manifestation of affinity the term auxiliary valency is proposed. Hence it is assumed that chemical affinity may act in the form of both principal and auxiliary valencies.

(c) On the Constitution of Substitution Compounds.

(a) Fundamental Considerations.

The compounds discussed in the foregoing pages were all members of the class known as addition-compounds.

But as well as these there also exists a large class of inorganic compounds, in the preparation of which essentially different phenomena are to be observed.

Thus, if triammintrinitrocobalt, the constitution of which already has been explained, is treated with ammonia a tetrammine compound, $Co(NO_2)_3(NH_3)_4$, is obtained. The examination of this tetrammin-salt shows that the introduction of the fourth ammonia molecule has caused a complete change in the functions of one of the nitro groups. In the triammin-salt all the nitro-groups are in the non-ionogene condition; but in the tetrammin-salt one of these groups is dissociable, and in its properties resembles the nitro-group in the alkali-nitrites. For example, weak acids are able, in aqueous solutions, to set free nitrous acid. Consequently, the entrance of the fourth ammonia molecule must have caused a change in manner in which the nitro-group was bound. This change can only be due to the ammonia replacing the nitro-group in its direct contact with the cobalt atom, as indicated in the equation:

$$(H_3N)_3C_0 < NO_2 + NH_3 = (H_3N)_3C_0 < NO_2 - NO_2 NO_2 + NO_2$$

A similar change has been noted in many other cases, e.g. in tetrachlorodiamminplatinate. The action of ammonia upon this compound causes one of the previously nonionizable chlorine atoms to become ionizable:

$$(\mathbf{H_3N})_2\mathrm{Pt} < \mathbf{Cl}^{\mathrm{Cl}}_{\mathrm{Cl}} + \mathbf{NH_3} = (\mathbf{H_3N})_2\mathrm{Pt} < \mathbf{Cl}^{\mathrm{Cl}}_{\mathrm{Cl}}$$

The supposition that the formation of the above compounds takes place when the ammonia replaces the acid radicle in its direct contact with the metal, finds considerable support in the agreement which exists between these addition reactions and the addition of ammonia to methyl iodide. In the latter case a non-ionizable residue becomes ionizable through the addition of ammonia, and the cause of this is generally assumed to be due to the ammonia coming between the carbon and iodine atoms which originally were directly bound together:

$$H C - I + NH_3 = H C - N)I$$

$$H C + NH_3 = H$$

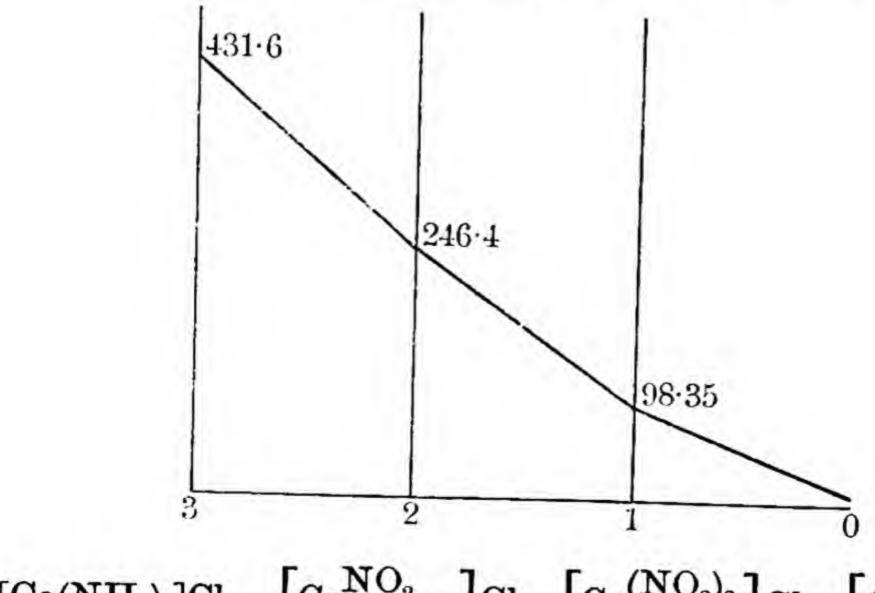
But all the acid residues in an inorganic compound may be replaced by ammonia, and in this way triammin-, tetrammin-, and hexamminplatinum salts are formed, and also tetrammin-, pentammin-, and hexammincobalt salts:

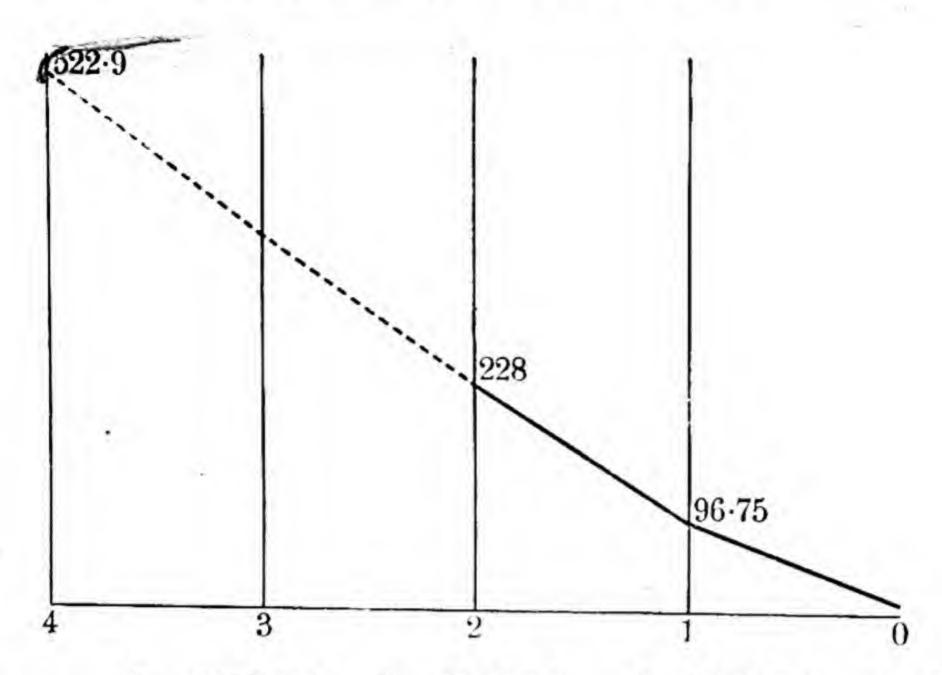
$$\begin{split} & \left[\mathrm{Co_{(NH_3)_4}^{(NO_2)_2}} \right] \mathrm{NO_2} + \mathrm{NH_3} = \left[\mathrm{Co_{(NH_3)_5}^{NO_2}} \right] (\mathrm{NO_2})_2 \\ & \left[\mathrm{Co_{(NH_3)_5}^{NO_2}} \right] (\mathrm{NO_2})_2 + \mathrm{NH_3} = \left[\mathrm{Co_{(NH_3)_6}^{NO_2}} \right] (\mathrm{NO_2})_3 \\ & \left[\mathrm{Pt_{(NH_3)_3}^{Cl_3}} \right] \mathrm{Cl} + \mathrm{NH_3} = \left[\mathrm{Pt_{(NH_3)_4}^{Cl_2}} \right] \mathrm{Cl_2} \\ & \left[\mathrm{Pt_{(NH_3)_4}^{Cl_2}} \right] \mathrm{Cl_2} + 2\mathrm{NH_3} = \left[\mathrm{Pt_{(NH_3)_6}^{Cl_2}} \right] \mathrm{Cl_2} \end{split}$$

The capacity of the compound to take up ammonia ceases when all the acid residues have passed into the so-called indirect combination.

The characteristic behaviour of these metallic ammonium compounds is exhibited not only in pure chemical reaction, but finds expression in their electrolytic conductivity, as will be evident from the following curves:

Molecular Conductivity at 1000 lts. Dilution.





The process of formation of substitution compounds may be followed most easily in the ammonium salts, which are characterized by great stability and very definite chemical properties. Yet it should be noted that not only ammonia, but also other compounds form salts by substitution. In this respect water deserves special mention, for it forms compounds which are completely analogous to those of ammonia. Examples in which this function of water may be convincingly demonstrated are—

$$\begin{bmatrix} Co_{(NH_3)_5}^{OH_2} \end{bmatrix} X_3 \qquad \begin{bmatrix} Co_{(NH_3)_4}^{(OH_2)_2} \end{bmatrix} X_3 \qquad \begin{bmatrix} Co_{(NH_3)_3}^{(OH_2)_3} \end{bmatrix} X_3$$

and many hydrates of metallic salts, of which only those of chromium, which have been thoroughly investigated, need be mentioned:

$$[Cr(OH_2)_6]Cl_8$$
 $[Cr_{(OH_2)_5}^{Cl}]Cl_2 + H_2O$ and $[Cr_{(OH_2)_4}^{Cl_2}]Cl + 2H_2O$

Sometimes very complicated molecules are able to exercise a function similar to ammonia and water; thus, for example, urea, in the hexauric chromium salts:

$$\left[\operatorname{Cr}\left(\operatorname{OC}_{\operatorname{NH}_2}^{\operatorname{NH}_2}\right)_{\!\scriptscriptstyle{6}}\right]\!X_{\scriptscriptstyle{3}}$$

Another example is found in the acetates of magnesium, prepared by B. N. Mentschutkin:

$$[Mg(CH_3 . COOH)_6]X_2$$
 $[Mg(C_2H_5COOH)_6]X_2$, etc.

Organic esters may also act in a similar way:

$$[Mg(CH_3 \cdot COOC_{3})_6]I_2$$
 $[Mg(CH_3 \cdot COOC_{2}H_5)_6]I_2$, etc.

(β) Generalizations deduced from the Constitution of Substitution Compounds.

The ammonium theory accounts for the formation of methylammonium iodide, from methyl iodide and ammonia, by assuming that the ammonia molecule interposes itself between the iodine and carbon atoms. It is usually supposed that the nitrogen becomes pentavalent, and that the iodine, in consequence of this change, leaves the carbon and unites with the nitrogen, thus:

$$\mathbf{H}_{3}\mathbf{C} \cdot \mathbf{I} + \mathbf{N} = \mathbf{H}_{3}\mathbf{C} \cdot \mathbf{N} \cdot \mathbf{I}$$
 \mathbf{H}_{3}

This conception when applied to analogous cases in inorganic compounds leads to very improbable results. Thus, for example, in the dinitrotetrammincobalt salts one ammonia molecule must be attached to cobalt in a different way to the remaining three—

$$H_3N$$
 C_0
 NH_3
 NO_2
 H_3N
 NO_2

and in the trichlorotriamminplatinum salts an ammonia molecule must be differently bound to the other two:

$$H_3N$$
 $Pt < Cl$ Cl Cl Cl

If this were true, then the number of isomers to be expected would be very great, but the behaviour of inorganic compounds in no way confirms this expectation, and accordingly until such confirmation is forthcoming, it is advisable to assume that every molecule of ammonia is attached to cobalt in the same way. This supposition is well supported by the chemical properties of these

addition compounds. Hence, the constitution of the above ammino complexes is best represented by the following formulæ:—

$$\begin{bmatrix} O_2N & NH_3 \\ O_2N & Co & NH_3 \\ NH_3 & NO_2 & and & \begin{bmatrix} Cl & NH_3 \\ Cl & Pt & NH_3 \\ NH_3 & NH_3 \end{bmatrix} Cl$$

The structural formulæ show that each ammonia molecule is bound to the central atom by auxiliary valencies, and that the negative residue outside the bracket is bound by an "indirect bond," a consequence of the interposition of ammonia.

The application of these ideas to methylammonium iodide gives us the following constitutional formula:—

As a result of these considerations, we propose a new hypothesis to explain the formation of methylammonium iodide, which can be expressed in the following words: The iodine atom, after it ceases to be directly bound to the carbon atom, still remains bound to carbon, and the nitrogen atom, in the addition compound, is bound to carbon by an auxiliary valency. The saturation of the iodine valency, which no longer can take place in the first sphere of attraction of carbon, since all the co-ordination positions are occupied, now takes place outside the first sphere.

The idea underlying the conception of an "indirect bond," is that the atom, by means of the interposition of ammonia, or groups which act in a similar way, is forced sufficiently far from the central atom to permit the interposing atom to come between the original pair. In this way the atoms in the second sphere still remain bound to the central atom, the only difference being that they no longer occupy a position in direct contact with that atom, but, owing to the interposition of ammonia or other molecules, take up a place in a separated zone.

Since the distance of these atoms from the central atom is of necessity greater than those directly bound, it is to be expected that such atoms will manifest certain peculiarities in their chemical behaviour. An idea of the nature of the characteristics to be expected is obtained when it is remembered that the elements with the greatest atomic volume (i.e. whose atomic centres after combination are furthest apart, such as the alkalis and halogens) have

the greatest tendency to the formation of ions. It is, therefore, possible to predict that those groups which are indirectly bound will be distinguished by their greater mobility, and in particular by their tendency to become ions. The facts confirm this expectation, so that all the characteristic properties of indirectly bound acid residues are expressed by all that is understood in the term "ionogene-binding."

It should be specially noted that it is impossible to determine by the customary methods the constitutional position of the indirectly-bound radicles, for such methods are incapable of giving an idea to which special atomic group in the molecule the ionogene radicles belong. On this account, when we desire to give expression in structural formulæ only to the atomic relationships which can be experimentally proved, we separate the ionogene groups by a bracket from the rest of the complex.

Both the metal ammonium salts which we have treated above are consequently given the following formulæ:—

$$\begin{bmatrix} \mathrm{Co_{(NO_2)_2}^{(NH_3)_4}} \end{bmatrix} \mathrm{NO_2} \quad \text{and} \quad \begin{bmatrix} \mathrm{Pt_{Cl_3}^{(NH_3)_3}} \end{bmatrix} \mathrm{Cl}$$

and methyl ammonium iodide similarly is written:

$$\left[\mathbf{C_{NH_{3}}^{H_{3}}} \right]$$
I

Which of the possible structural solutions of the latter formulæ:

$$I(H_3C-NH_3)$$
 or H_3C-N-I or $H_3C-N-HI$ H_3

is the most probable, is impossible to decide experimentally, and it appears in general doubtful whether we are justified in asking for such a solution. I incline to the opinion that we are not. For we can very well conceive that the iodine atom in methylammonium iodide in virtue of its great mobility and ionogene properties can assume the most diverse positions with respect to the complex (H₃C—NH₃), so that it is impossible to ascribe to the compound any definite structure. Similar phenomena are met with in tautomeric hydrogen compounds.

We have, therefore, to think of the radicle (H₃C . NH₃) as a whole, and as still possessing an unsaturated valency.

(d) On the Number of Auxiliary Valencies on an Atom.

The laws governing the saturation of the principal and auxiliary valencies of elementary atoms exhibit complete agreement. For just as the number of principal valencies determine the number of monovalent groups which an atom is able to attach to itself, so in like manner the number of auxiliary valencies determine the number of molecules to be attached to the central atom. Boron, in trimethyl boron, has one unsaturated auxiliary valency, and consequently is able to take up one molecule of ammonia, thus forming trimethyl ammonium borate:

$$\begin{array}{c} CH_{3} & CH_{3} \\ H_{3}C - B - + - NH_{3} = H_{3}C - B - NH_{3} \\ CH_{3} & CH_{3} \end{array}$$

This salt is very stable, and yields very beautiful crystals.

The central atoms of platinum chloride and tin triethyliodide possess two free auxiliary valencies, and combine with two molecules of ammonia to form the compounds—

In thallium chloride, cobalt nitrite, etc., the central atoms have three unsaturated auxiliary valencies, and consequently take up three molecules of ammonia, or amine—

But the activity of the auxiliary valencies has not yet reached its limit, for in many cases still further molecules may be attached to the complex, thus forming substitution compounds.

Nevertheless, the composition of compounds of the higher order teaches that the number of auxiliary valencies on the central atom is not unlimited, but like the principal valencies exhibits a maximum. This maximum value may be obtained from the composition

and constitution of the limiting types of the substitution compounds.

Examples of the limiting compounds of different elements, chosen from the ammonium group because these compounds have been most carefully studied, are as follows:—

$$[\text{Co(NH}_3)_6]X_3$$
, $[\text{Ni(NH}_3)_6]X_2$, $[\text{Pt(NH}_3)_6]X_4$, $[\text{Ir(NH}_3)_6]X_3$, $[\text{Rh(NH}_3)_6]X_3$, $[\text{Co en}_3]X_3$, $[\text{Fe Dipy}_3]X_2$, $[\text{Cr en}_3]X_3$, $[\text{Ni en}_3]X_2$, $[\text{Zn en}_3]X_2$, $[\text{Cd en}_3]X_2$.

¹ Pfeiffer, Zeitsch. anorg. Chem., 24, 279 (1900).

² Ethylendiamine (en) and dipyridyl (dipy), since they are diamines, are equivalent to two molecules of ammonia.

These examples show that the limiting value of the auxiliary valencies of many elements is six; nevertheless in some cases this value is only four. The meaning of this surprising result, viz. that the number of the auxiliary valencies of many elements is six, will become clear to us in the next chapter when discussing another characteristic numerical conception of the elementary atom.

The only question which at present interests us is the number of auxiliary valencies, besides the maximum value, which an atom can exhibit. In reference to this point, it may be stated that the auxiliary valencies very often only are active towards definite molecular complexes, and hence the formation of addition compounds with other classes of molecules is impossible. Consequently the number of auxiliary valencies which are active towards different molecules is not always the same. Considering the extraordinary variety in composition exhibited by substitution compounds it is not surprising that the number of auxiliary valencies on the atom are variable.

The accurate determination of the maximum value is difficult, because the molecular weight of most of the compounds is unknown. Consequently it is impossible to decide whether auxiliary valencies take part in the polymerization of the molecule, thus bringing into play a greater number of auxiliary valencies than is at first apparent. The following example may serve to make these points clear: PtCl₂ takes up one molecule of PCl₃. If the compound possessed the simple formula Cl Pt. PCl₃, then only one auxiliary valency

of platinum would be active. Rosenheim and Löwenstamm have shown, however, that the compound is bimolecular, and has in consequence one of the following formulæ:—

in which two auxiliary valencies of platinum take part. Consequently it is obvious that before the question of the variable nature of auxiliary valencies can receive an adequate treatment much experimental material on the molecular weight of complex compounds must be prepared.

3. The Co-ordination Number.

(a) Definition of the Co-ordination Number.

Atoms which are directly attached, either by principal or auxiliary valencies, to another atom, are in the first or undissociable zone. They may also be bound to other atoms, and with respect to the latter they may be in the second or dissociable zone, but in such a case they fall outside the following discussion. It is only of importance to the theoretical treatment of compounds of the higher order to determine how many atoms are in the first zone. The number which expresses this is called the "Co-ordination number." Of the possible values which the co-ordination number of an element may have, only the maximum value is at present of interest.

By the term "maximum value" is to be understood that value which expresses the maximum number of atoms which can exist in direct combination with the central atom.

Those compounds in which the co-ordination number has been reached are said to be "co-ordinatively saturated." There are many well-characterized compounds which are co-ordinatively unsaturated, i.e. the maximum co-ordination number has not been attained. Although the theoretical treatment of co-ordinatively saturated compounds is already far advanced, that of the unsaturated is still only in its infancy. Consequently in what follows those compounds which are co-ordinatively saturated will receive most attention.

1 Zeitsch. anorg. Chem., 37, 394 (1903).

(b) The Determination of the Maximum Co-ordination Number.

The maximum value of the co-ordination number of an elementary atom can be obtained from its compounds, the constitution of which has been determined, viz. from the maximum number of atoms, radicles, and groups linked to the central atom. The ammonium salts of many metals have proved to be the most satisfactory for this determination, but other classes of compounds of the higher order may also be used, e.g. hydrates, and other complex salts; the results in these cases are not so trustworthy.

It has been found: 1. That the maximum co-ordination number is practically independent of the nature of the central atom. The following examples illustrate this:—

$$\begin{split} & [\mathrm{Co(NO_2)_6]R_3,^1} \quad [\mathrm{Co(CN)_6]R_3,^2} \quad \Big[\mathrm{Co}_{(\mathrm{OH})_2}^{\mathrm{Fl_4}}\Big] (\mathrm{NH_4)_2,^3} \\ & \Big[\mathrm{Co}_{(\mathrm{NO_2)_4}}^{\mathrm{(NH_3)_2}}\Big]\mathrm{R,^4} \quad [\mathrm{Co(NH_6)_3]X_3,^5} \quad [\mathrm{Co(OH_2)_6]Cl_2,^6} \quad [\mathrm{PtCl_6]R_2,^7} \\ & \Big[\mathrm{Pt}_{\mathrm{Cl_5}}^{\mathrm{NH_3}}\Big]\mathrm{R,^8} \quad \Big[\mathrm{Pt}_{\mathrm{Cl_4}}^{\mathrm{(NH_3)_2}}\Big],^9 \quad \Big[\mathrm{Pt}_{(\mathrm{CN})_4}^{\mathrm{Cl_2}}\Big]\mathrm{R_2,^{10}} \quad \Big[\mathrm{Pt}_{(\mathrm{CN})_4}^{\mathrm{Br_2}}\Big]\mathrm{R,^{11}} \\ & [\mathrm{Pt(NH_3)_6]X_4,^{12}} \quad [\mathrm{Pt}(\mathrm{SCN})_6]\mathrm{R_2,^{13}} \quad \mathrm{etc.} \end{split}$$

- ¹ N. W. Fischer, Pogg. Ann., 74, 124 (1848); St. Evre, Comp. rend., 33, 166 (1851).
- ² C. Zwenger, Annalen, **62**, 157 (1847); O. T. Christensen, J. pr. Chem., (2) **31**, 163 (1885).

³ R. Wagner, Ber., 19, 896 (1886).

4 O. L. Erdmann, J. pr. Chem., 97, 385 (1866).

⁵ S. M. Jörgensen, Zeitsch. anorg. Chem., 17, 455; 19, 78 (1899).

6 Brooke, Ann. Phil., 23, 364; C. Marignac, Rech. sur les formes crist. Genève, 1855, 19.

7 O. Dammer, III. Bd., Handbuch d. anorg. Chem.

8 A. Cossa, Ber., 23, 2508 (1890).

⁹ C. Gerhardt, Comp. rend., 1850, 273; Annalen, 76, 307 (1850).

10 W. Kopp and G. Schnedermann, J. pr. Chem., 37, 461 (1846); E. A. Hadow, Jahresber. chem., 1860, 226.

11 N. O. Holst, Bull. Soc. Chim., (2) 22, 347 (1874).

12 B. Gerdes, J. pr. Chem., (2) 26, 257 (1882).

- 13 G. B. Buckton, Soc. Quart. Journ., 7, 22; J. pr. Chem., 64, 65 (1855).
- 2. That in a very great number of elements the maximum coordination number is six. The following examples illustrate this point, as well as those given above:—

$$\begin{split} & [Pt(Br_6)]R_{2},^1 \quad [CrCy_6]R_{3},^2 \quad [Cr(SCN_6)R_{3},^3 \quad \Big[Cr\frac{(NH_3)_2}{(SCN)_4}\Big]R,^4 \\ & \Big[Pt\frac{(NH_3)_2}{Cy_4}\Big],^5 \quad [IrCl_6]R_{2},^6 \quad [FeCy_6]R_{4},^7 \quad [FeCy_6]R_{3},^8 \\ & \Big[Fe\frac{NO}{Cy_5}\Big]R_{2},^9 \quad [FeF_6]R_{3},^{10} \quad [Ru(NO_2)_6]R_{3},^{11} \quad [AlF_6]R_{3},^{12} \\ & [SiF_6]R_{2},^{13} \quad \Big[Ru\frac{NO}{Cl_5}\Big]R_{2},^{14} \text{ etc.} \end{split}$$

¹ W. Halberstadt, Ber., 17, 2962 (1884).

² O. T. Christensen, J. pr. Chem., (2) 31, 165 (1885).

³ J. Rösler, Annalen, 141, 185 (1867).

⁴ A. Reinecke, Annalen, 126, 113 (1863); O. Nordenskjöld, Zeitsch. anorg. Chem., 1, 135 (1892).

⁵ Th. Wilm, Ber., 22, 1542 (1889).

⁶ J. J. Berzelius, Pogg. Ann., 13, 435, 527; 15, 208 (1829); F. Wöhler, ibid., 31, 167 (1834); C. Claus, J. pr. Chem., 39, 102 (1846).

⁷ Dammer, Handbuch d. anorg. chem., III. Band.

8 Ibid.

Playfair, Annalen, 84, 317 (1852); K. A. Hofmann, Annalen, 312, 1 (1900).
 P. T. Walden, Zeitsch. anorg. Chem., 7, 331 (1894).

11 C. Claus, Jahresber., 1863, 697; E Leidié, Compt. rend., 111, 106 (1890).

¹² H. Deville, ibid., 42, 49; Ann. chim., (3) 49, 19 (1857); J. pr. chem., 67, 367 (1856).

13 J. J. Berzelius, Pogg. Ann., 1, 172 (1824).

14 A. Joly, Compt. rend., 107, 994 (1888).

(c) Values of the Maximum Co-ordination Number.

We have seen that the co-ordination number of many elements is six, and the question naturally arises as to whether the maximum co-ordination number is always six. The reply is in the negative. The examination of the compounds of carbon afford the best illustration of this fact, for, as is well known, the number of atoms which can be directly linked to carbon never exceeds four. The maximum co-ordination number of carbon is consequently four. The values of the maximum co-ordination number and that of the principal valencies is, therefore, the same, and it is due to this fact that a differentiation between the two conceptions was not made earlier. But if the maximum co-ordination number of carbon is four, it is natural to expect that other elements would have the same number. This expectation is fulfilled, for it is found that those elements which occupy positions next to carbon in the periodic system have four as their maximum co-ordination number. Boron, a more positive element than carbon, and nitrogen, a more negative

element, are good examples. Both boron and nitrogen are trivalent, according to their hydrogen, BH₃ and NH₃, and chlorine compounds, BCl₃ and NCl₃. If they possess four as their maximum co-ordination number, then they ought to form the complex radicle MR₄, when R is a monovalent group. The facts are in complete agreement with this prediction, as the existence of hydrofluoboric acid and the salts of ammonia show:

$$F \\ F \\ B \cdots FH \quad and \quad H \\ N \cdots HX$$

We consequently arrive at the following conclusions: The numerical value of the maximum co-ordination number and of the principal valencies is the same in the case of carbon. Such behaviour is exceptional. The maximum co-ordination number of carbon and of its neighbouring elements is four, while on the other hand, this value is six for the vast majority of the other elements.

It appears probable that in a few elements the maximum coordination number can rise as high as eight; for molybdenum gives rise to the compound (MoCy₈)K₄, which is stable in aqueous solution. Further, the addition products of the chlorides of the alkaline earths: CaCl₂(8NH₃),¹ SrCl₂(8NH₃),² BaCl₂(8NH₃),³ and the chlorides of zirconium and thorium, ZrCl₄(8NH₃)₄, ThCl₄(8NH₃),⁴ are, possibly, to be placed in the same class.⁵

(d) On the Co-ordination Number of Polyvalent Atoms and Atomic Groups.

It is of considerable importance to know whether a divalent atom occupies one or two co-ordination positions. Information on this point is obtained from the examination of those radicles which contain divalent atoms. Should a divalent atom lay claim to two co-ordination positions, then the radicle MR_6 (R being a monovalent atom or group) would take the form $M_{R^4}^{R'}$ (R' being a divalent

¹ H. Rose, Pogg. Ann., 20, 165 (1830).

² Ibid., p. 154.

³ A. Joannis, Compt. rend., 112, 337 (1891).

⁴ J. M. Mattheus, J. Amer. Chem. Soc., 20, 815 (1898).

A more recent examination of some of these compounds has shown that some, at any rate, are mixtures of metallic amides and ammonium chloride.

atom), i.e. the limiting type of a complex radicle in the formation of which, for example, both oxygen and fluorine took part, must be of the form $M \stackrel{O}{:} F_4$. This, however, is not the case, as the following examples show:—

$$\begin{bmatrix} VF_{6}]K_{3},^{1} & \begin{bmatrix} V^{O}_{\mathbf{F}_{5}} \end{bmatrix}K_{2},^{1} & \begin{bmatrix} V^{O}_{\mathbf{F}_{5}} \end{bmatrix}(NH_{4})_{2},^{1} & \begin{bmatrix} Mo^{O}_{\mathbf{F}_{5}} \end{bmatrix}(NH_{4})_{2},^{2} \\ \begin{bmatrix} Nb^{O}_{\mathbf{F}_{5}} \end{bmatrix}(NH_{4})_{2},^{3} & \begin{bmatrix} W^{O_{2}}_{\mathbf{F}_{4}} \end{bmatrix}(NH_{4})_{2},^{4} & \begin{bmatrix} Mo^{O_{2}}_{\mathbf{F}_{4}} \end{bmatrix}(NH_{4})_{2},^{5} \\ \begin{bmatrix} V^{O_{2}}_{\mathbf{F}_{4}} \end{bmatrix}(NH_{4})_{3},^{6} & \begin{bmatrix} W^{O_{3}}_{\mathbf{F}_{3}} \end{bmatrix}(NH_{4})_{3},^{7} & \begin{bmatrix} Mo^{O_{3}}_{\mathbf{F}_{3}} \end{bmatrix}(NH_{4})_{3},^{8} \\ \end{bmatrix}$$

¹ Em. Petersen, Ber., 21, 3258 (1888).

² F. Mauro, ibid., 15, 2510 (1882); Gaz., 19, 179 (1888).

³ C. Marignac, Ann. Chim. Phys., (4) 8, 34 (1866).

4 Ibid., (3) 69, 65 (1863).

5 Delafontaine, Arch. Sci. phys. nat., 30, 240.

⁶ Em. Petersen, Ber., 21, 3259 (1888).

⁷ C. Marignac, Ann. Chim. Phys., (3) 69, 65 (1863).

⁸ F. Mauro, Zeitsch. anorg. Chem., 2, 25 (1892).

The composition of these compounds shows that divalent atoms, as well as other atoms, occupy only one co-ordination position. The same conclusion is to be deduced from the composition of the limiting types of the oxygen and sulphur salts:

In agreement with the behaviour of the other elements, it is found that trivalent elements also only occupy one co-ordination position, as may be seen in the salts of nitrilopentachloroosmic acid.¹

$$\left[\mathrm{Os}_{\mathrm{Cl}_{5}}^{\mathbf{N}}\right]\mathrm{R}_{2}$$

On the other hand, polyvalent radicles composed of several atoms, as for example the residues of oxalic, carbonic, and sulphuric acids, etc., behave differently from polyvalent atoms. In these radicles the free valencies being on different atoms are consequently separated spacially, and hence, on saturation, such radicles occupy one or more co-ordination positions. This is true of CO₃ and

¹ A. Werner and K. Dinklage, Ber., 34, 2698 (1901).

C₂O₄ in the following compounds, the structural formulæ of which may be written thus:

$$\begin{bmatrix} OC_O^O : Co(NH_3)_4 \end{bmatrix} X^{\ 1} \quad and \quad \begin{bmatrix} CO_2 : \\ | \\ CO_2 : \end{bmatrix} Co(NH_3)_4 X^{\ 2}$$

¹ S. M. Jörgensen, Zeitsch. anorg. Chem., 2, 282 (1892).

² Ibid., 11, 429 (1896).

In constitution and chemical behaviour such compounds are completely in agreement with the diacidotetrammin salts $[X_2Co(NH_3)_4]X$. Just as the action of ammonia on the latter compounds causes an acid residue to become indirectly bound to cobalt:

$$X \left[(H_3N)_4 Co \left\langle \begin{array}{c} X \\ X \end{array} \right] + NH_3 = X \left[(H_3N)_4 Co \left\langle \begin{array}{c} NH_3 \\ X \end{array} \right] X$$

so, in like manner, the entrance of ammonia into the carbonatotetrammin salts causes a similar change to take place to one of the valencies of the acid residue:

³ A. Werner, Ber., 36, 2378 (1903).

In this compound the polyvalent acid residue, which is now only bound by one direct bond to the cobalt atom, is just as indissociable as it was in the original carbonatotetrammin salt. From these results it is to be concluded that polyvalent acid residues, built up from several atoms, occupy one or more co-ordination positions.

The following compounds contain polyvalent acid residues occupying only one co-ordination position:

$$\begin{split} & \left[\begin{array}{ccc} Co_{(NH_3)_5}^{SO_4} \right] X,^1 & \left[Co_{(NH_3)_5}^{CO_3} \right] X,^2 & \left[Co_{(NH_3)_5}^{C_2O_4} \right] X,^3 \\ & \left[\begin{array}{ccc} HO_{\circ} \\ O_4S \end{array} \right] Pt(NH_3)_4 \right] X,^4 & \left[\begin{array}{ccc} Br \\ O_4S \end{array} \right] Pt(NH_3)_4 \right] X,^4 & \left[\begin{array}{ccc} Br \\ O_4S \end{array} \right] Pt(NH_3)_4 \right] X,^4 & \left[\begin{array}{ccc} O_3N \\ O_3C \end{array} \right] Pt(NH_3)_4 \right] X,^4 & \left[\begin{array}{ccc} O_3N \\ O_3P \end{array} \right] Pt(NH_3)_4 \right]^4 \end{split}$$

¹ S. M. Jörgensen, J. pr. Chem., (2) 34, 262 (1885).

² A. Werner and N. Goslings, Ber., 36, 2378 (1903).

³ S. M. Jorgensen, Zeitsch. anorg. Chem., 11, 1418 (1903).

P. T. Cleve, K. Sv. Akad. Handl., 10, No. 93.

On the other hand, we have, in the following compounds, examples of polyvalent acid residues occupying two co-ordination positions:

$$[O_3C \cdot Co(NH_3)_4]X,^1$$
 $[C_2O_4 \cdot Co(NH_3)_4]X,^2$ $[C_2O_4Co\ en_2]X,^3$ $[O_4S \cdot Pt)NH_3)_4]X_2,^4$ etc.

¹ S. M. Jörgensen, Zeitsch. anorg. Chem., 2, 282 (1892).

² Ibid., 11, 429 (1896).

3 A. Werner and A. Vilmos, Zeitsch. anorg. Chem., 21, 145 (1899).

⁴ P. T. Cleve, Om Ammoniakalkische Platina Föreningen, 1866, p. 72.

And hence it is quite certain that polyvalent acid residues, just like other radicles, may be directly attached to the central metallic atom.

(e) On the Actual Meaning of the Maximum Co-ordination Number.

It has been shown that the maximum co-ordination number of the vast majority of those elements for which it was possible to accurately obtain this value is six, and that only a few of the elements, members of the second group in the periodic system, viz. those with the smallest atomic volume, had the lower value of four. From these facts it is to be concluded that this numerical conception of the affinity content of an atom is, within wide limits, independent of the size of the atom. If this be true, then the maximum co-ordination number must be considered as having reference to the space around the surface of the atom, i.e. it is a numerical conception which expresses the number of atoms which can arrange themselves in the first sphere of attraction of another atom. This idea leads to many inferences, which can be confirmed by experiment. In the first place, we may mention carbon as illustrating this point. The maximum co-ordination number of this element is four, and, according to the theory of Van't Hoff and Le Bel, four atoms can group themselves in a symmetrical manner around the central carbon atom. The same is true of the ammonium compounds:

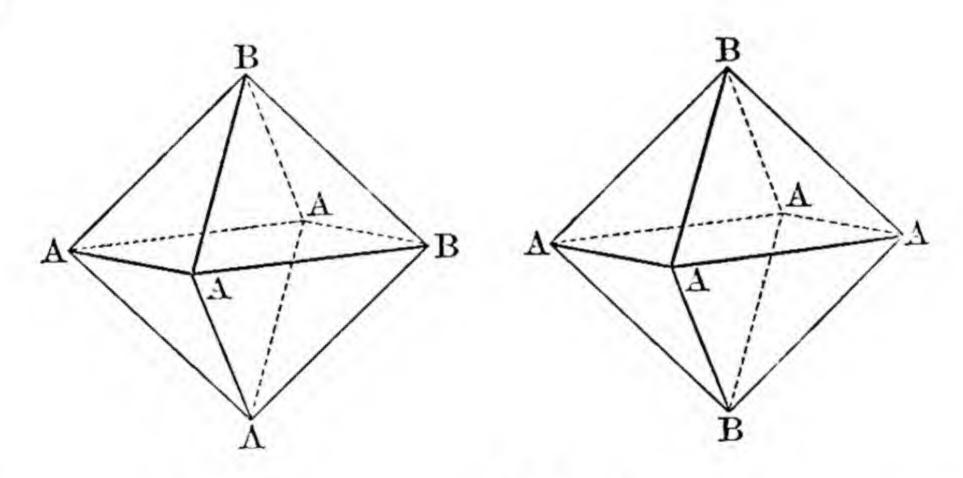
$$\begin{pmatrix} R_1 \\ N_{R_2}^{R_2} \\ R_4 \end{pmatrix} X$$

in which four groups are bound to the co-ordinatively saturated

nitrogen atom. The isomeric phenomena of these compounds correspond to the tetrahedral position which these groups occupy around the nitrogen.

The characteristic difference between the carbon compounds CX_4 and the analogous ones of other elements, viz. SiX_4 , SnX_4 , PbX_4 , supports the spacial explanation of the maximum coordination number. The compounds of carbon, in opposition to those of other elements, are unable to form addition compounds; they can only form substitution compounds, e.g. carbon tetrachloride forms no chloro-salts, and carbon tetrabromide no bromo salts, etc.

The six corners of a regular octahedron represent the symmetrical positions which six atoms would take up around the central atom, the maximum co-ordination number of which was six. This octahedral position admits of two different spacial possibilities when the six co-ordinated groups are different, as in the complex $\begin{bmatrix} M & A_4 \\ B_2 \end{bmatrix}$ thus:



Compounds with the complex $M_{\rm B_2}^{\rm A_4}$ should therefore exist in two isomeric forms. It has been possible to confirm this important deduction in the case of three elements: platinum, cobalt, and chromium. The maximum co-ordination number, when considered spacially, provides a means by which a very great number of phenomena may be grouped together, and is the first clear explanation to give any idea of the combining possibilities of the atom. Moreover, the maximum co-ordination number is a working hypothesis of great value, because by it we are enabled to predict the type of compound to be expected on combining compounds of the first order.

4. The Number of Auxiliary Valencies.

A phenomenon, differing essentially in its character from those which we have already studied, is to be observed in the formation of a series of molecular compounds, viz. the transformation of acid residues from the non-ionized into the ionized condition before all the co-ordination positions are filled. Platinous chloride, for example, takes up two molecules of ammonia, amine, phosphine, sulphide, selenide, etc., without affecting its chlorine atoms; but as soon as a third molecule of one of these compounds is taken up, one chlorine atom becomes ionized; and when a fourth molecule is added, the second chlorine likewise becomes an ion. Consequently, before the six co-ordination positions of platinum are occupied, the chlorine atoms, which originally were non-ionogenes, have become ionogenes. Paladium chloride behaves similarly. V. Kohlschütter¹ showed that the introduction of the third thiocarbamide residue into the thiocarbamide compounds of monovalent platinum was followed by the transformation of the acid residue from the non-ionogene into the ionogene condition. In all such cases the resulting compounds, as for example:

$$\left[\text{Pt}^{\text{Cl}}_{(\text{NH}_3)_3} \right] \text{Cl}, \quad \left[\text{Pt}(\text{NH}_3)_4 \right] \text{Cl}_2, \quad \left[\text{Pd}(\text{NH}_3)_4 \text{Cl}_2, \quad \left[\text{Cu} \left[\text{SC}(\text{NH}_2)_2 \right]_3 \right] \text{Cl} \right]$$

behave as if the central atom was co-ordinately saturated, while in reality this is not the case. The divalent platinum compounds are particularly suited to illustrate this fact. Thus, for example, tetrahydroxylaminplatohydroxide may be formed from the chloride, and has in consequence the formula:

And further, the tetramminplato compounds can, under certain conditions, take up still another molecular component, a fact made evident in the following structural formula:

$$\left[Pt_{(NH_3)_2}^{(NH_2C_6H_5)_3} \right] SO_4^2$$

² Cleve, On Ammoniacal Platinum Bases, 76 (1872).

The transformation of the acid residue from a non-ion to an ion therefore cannot, as was the case in the substitution compounds,

¹ Annalen, 349, 232 (1906).

be considered as resulting from the interposition, due to complete co-ordinative saturation, of the substituents between the central atom and the acid residue. The transformation consequently must be effected by some other factor.

The following words, which are as free as possible from unlikely assumptions, sum up these changes: After the saturation of a definite number of auxiliary valencies, each further addition of a molecular component takes place in such a way as to cause a principal valency to transmit ionic properties to the acid residue attached to it. The number of auxiliary valencies which are saturated, when the first acid residue receives ionogene properties, is called the "ionogene auxiliary valency number." This number is different in different elements, and probably varies with the nature of the molecules which become attached by the secondary valencies.

III. On the Units of Valency.

1. Introduction.

Just as the new structural formulæ of molecular compounds require an increase in the saturation capacity of most elementary atoms, so, in like manner, must the number of valencies which come into action on the atom undergo a like increase. The extension of the doctrine of valency which thus becomes necessary is, on this account, quite comparable with the change from the conception of constant to that of variable valency. But the units of valency formerly ascribed to the atom were of the same kind as those already existing on the atom, whereas those now proposed, as a result of our deductions on co-ordination formulæ, differ from those already on the atom, inasmuch as they bind quite different radicles. Consequently a difference must be made in the names which are given to these two manifestations of affinity, and it is proposed to call them principal (or primary) valencies, and auxiliary (or secondary) valencies.

The following paragraphs are intended to make clear the difference between principal and auxiliary valencies.

2. Definition of Principal and Auxiliary Valencies.

For the present only the chief differences between these two types of valency can be given, for the more accurate definition can be properly understood only when a knowledge of their relationships to one another and of the peculiar phenomena attending their saturation has been described. When we confine ourselves solely to the experimental facts—as far as we at present know them—principal and auxiliary valencies may be defined as follows:—

- 1. Principal valencies are manifestations of affinity, which permit their saturation capacities to be measured in terms of hydrogen atoms or groups equivalent to the latter.
- 2. Auxiliary valencies are manifestations of affinity which bring about the stable union of radicles; the latter being able themselves to exist as independent molecules.

Thus principal valencies are able to bind:

$$-Cl$$
, $-Na$, $-NO2$, $-CH3$, etc.

Auxiliary valencies are able to bind:

3. The Unit of Valency considered as a Directed Independent Force.

(a) General remarks.

The fact that an atom is able to combine with a definite maximum number of other atoms is even to-day, in many cases, interpreted as meaning that the affinity of an atom only comes into action through a definite number of units of valency which are considered as independent forces (einzelkräfte). According to this conception the unit of valency consists of a fraction of the affinity of the atom appearing as an independent force, and acting so as to hold together two atoms, thus forming a molecule. Some experimenters further assume that these independent forces (units of valency) only act from definite positions on the surface of an atom, and polyvalent atoms therefore have their units of valency separated and assigned to definite points on their surfaces. Other workers have added the hypothesis that the units of valency can act only in definite directions in space. Thus, for example, the four valencies

In the following discussion only the principal valencies receive consideration, because the auxiliary valencies are less suited to such treatment.

Erlenmeyer, Lehrbuch der organischen Chemie, p. 40.
 Van't Hoff, La chimie dans l'espace, 1875.

of carbon are supposed to act in the direction of the four corners of a regular tetrahedron, the carbon atom being at its middle point.

The hypothesis, that units of valency are independent forces, forms the basis of many of the present-day theories, particularly those which deal with steric-hindrance. This conception of the unit of valency contains in it more than may logically be deduced from the facts, requires hypotheses on the internal structure of the atom, and presents problems which, in spite of much work and trouble, have not as yet been solved.¹

For example, it presupposes that definite positions on polyvalent atoms are different from others; it requires the relative positions of these differing points to be indicated; it asks in what direction and at what angle the units of valency act; and, in short, requires a definite picture of the configuration of the atom.

Lossen³ has recognized the difficulties of the theory which ascribes to the unit of valency an individual existence, and has written against such a conception in his paper "Über die Verteilung der Atome in der Molekel." He defines valency from the facts and without the introduction of any hypothesis in the following words: "The value (valency) of an atom is a number which expresses how many atoms are present in its combining zone. Since the number of atoms directly bound to a polyvalent atom varies, so is the value of such a polyvalent atom variable." A. Claus has expressed similar views. He says, "The hypothesis that valency in polyvalent atoms is a pre-existing force acting with definite units of affinity is just as unfounded as it is unnatural."

It is therefore obvious that a series of reasons may be brought forward to disprove the supposition that valency manifests itself in independent forces on an atom. A further argument against such a theory is to be found in the phenomenon already exhaustively discussed in the foregoing pages, viz. that valency can exhibit every possible value below the maximum. For were the theory true, then we should have a number of unsaturated independent forces on the majority of the elementary atoms in most compounds, provided that the additional, unproved hypothesis of mutual saturation was not introduced.

¹ Wunderlich, Konfiguration organ. Moleküle, p. 8.

² Lossen, Ann. Chem. u. Pharm., 204, 327 (1880).

³ *Ibid.*, **204**, 265 (1880).

⁴ Ibid., 204, 284 (1880).

⁵ Ber., 14, 432 (1881).

The most weighty objections to the theory of individual valencies are to be deduced from the behaviour of certain carbon compounds, because the phenomena resulting from the valency conditions in organic compounds is best characterized—a result to be directly referred to the high state of development attained in organic structural formulæ. The examination of these phenomena discloses a series of simple changes for which we might seek an explanation in vain were we to suppose that valency acts only at definite points on the atom, while on laying aside such a supposition a satisfactory explanation may be obtained. Phenomena of this description are met with in the racemization of optically active compounds, and in compounds with polybound carbon atoms, e.g. in the transformation of geometrical isomers. Some of these phenomena will receive a short treatment in the following paragraphs.

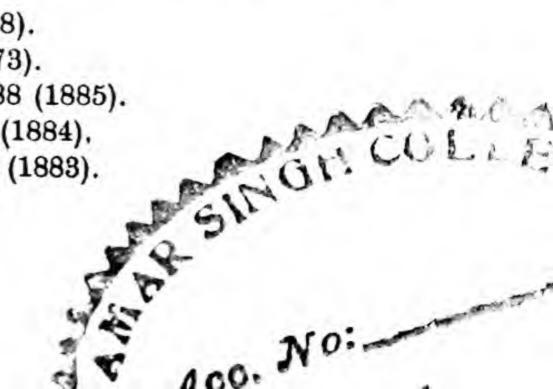
(b) Objections to the Theory that Valency is a Directed Individual Force.

(a) Racemization of Optically Active Compounds.

It is well known that all optically active compounds may be transformed into their inactive modifications. This change may be illustrated by the following examples. Optically-active amyl alcohol on heating yields the inactive alcohol. The same change is brought about by warming with caustic soda; it even takes place during the preparations of the active form. Heat transforms active lactic acid into the inactive form. Leucine, when heated with baryta-water to 166°, passes into inactive leucine; a similar change takes place when aspartic acid is heated 170–180° with any salt of hydrochloric acid. The active mandelic acids pass into the inactive acids when heated to 180°, etc.

Lewkowitsch in the following words has called attention to the difficulties experienced in giving a satisfactory explanation of such racemization: "Although the transformation of paramandelic acid into both active isomers is easily explained by Van't Hoff's

d Ibid., 16, 2722 (1883).



¹ Le Bel, Compt. rend., 87, 213 (1878).

² Wislicenus, Annalen, 167, 318 (1873).

Schulze and Bosshard, Ber., 18, 388 (1885).
 Michael and Wing, ibid., 17, 2984 (1884).

⁵ Lewkowitsch, ibid., 16, 1575, 2722 (1883).

hypothesis, the explanation of the reverse change offers considerable difficulty." This is indeed true, for when explaining this change with the help of the theory of separated units of valency, we must assume that under the influence of the reagents either the radicles change their places or the units of valency themselves, together with the radicles attached to them, must change their places. The former supposition would require the individual radicles, for a short interval of time, to be loosed from the carbon atoms, with the result that it ought to be possible, under the experimental conditions, for them to combine with one another to form stable molecules. Hence in the racemization of optically active bodies, by-products should be formed; an inference which finds no experimental support, for such reactions generally go very smoothly. If, on the other hand, it is assumed that the units of valency can change their places in company with the radicles attached to them, then, since these units of valency are themselves linked to definite parts of the atom, it must also be assumed that these parts of the atom are able to change their positions with respect to one another. Hence the material composing the atoms must, to a certain extent, be mobile, an assumption which, without a more certain foundation, would seem improbable.

(B) Unsaturated Linkings.

The properties of unsaturated compounds are in opposition to the conception that valency consists of unchangeable and individual forces, as will be made clear by the following considerations. The original idea of poly bonds took as its foundation the supposition that two atoms could be bound to one another not only by one but also by several single bonds (valencies). The behaviour of such compounds contradicts the idea of such a strengthening of atomic-bindings, for doubly bound atoms are more chemically active than those which are only singly bound, since the conditions have, up to the present, been most thoroughly worked out in the compounds of carbons, and as the conclusions thus reached are applicable to inorganic compounds, the following discussion will be treated from the point of view of the carbon compounds.

Carbon atoms linked together by several bonds usually exhibit an increased reactivity, i.e. they evince an unsaturated condition as if the formation of these double bonds caused the saturation of the molecule to become incomplete, saturation only being restored by the addition of certain components. The most suitable name for such double bonds is therefore "Incomplete-bonds" ("Lücken-bindung").

The want of agreement between the structural formulæ and the behaviour of compounds with double bonds has caused it to be denied that double bonds exist. Lossen writes, "I call oxygen divalent because in its combining zone two atoms of hydrogen, two of carbon, or, in short, any two atoms can exist. An atom cannot be twice in the combining zone of a carbon atom; to assume that is nonsense. My way of considering the matter knows no double bonds on poly-valent atoms." F. W. Hinrichsen 2 has also written against the conception of double bonds. According to this author, all elementary atoms which have not yet attained their maximum valency in their compounds are unsaturated, and consequently ethylene and acetylene compounds are simply special examples of unsaturated compounds. The opinion of Hinrichsen in this simple form is untenable, for if unsaturated bonds exist in ethylene, why should we not be able to prepare such compounds as ethyl, CH₃. CH₂—; ethylidene, H₃C. CH=; or unsaturated trimethylene, $CH_2 < \frac{CH_2}{CH_2}$ Consequently for just those compounds in which such "incomplete bonds" are most in evidence, those in which the unsaturated valencies are on neighbouring atoms, is the explanation of Hinrichsen most wanting.

In order to bring about a more satisfactory agreement between the behaviour of compounds containing double bonds and the structural picture of the same, special suppositions on the nature of double bonds have been brought forward. The best known of these is that known as Baeyer's tension theory. According to this theory the valencies which originally were directed outwards from the corners of a regular tetrahedron become forced from this position and thus have a tendency to return to their first state. In this way Baeyer explains the fact that the carbon atoms in ethylene compounds, in spite of being doubly bound, are less firmly joined than those which are linked together by single valencies. Against this mechanical picture, which compares ethylene linkings to strained springs, several objections have been raised. Thus, for

¹ Annalen, 204, 295 (1880).

Hinrichsen, Über den gegenwärtigen Stand der Valenzlehre, p. 223.
A. v. Baeyer, Ber. 18, 2277 (1885).

example, it has been pointed out 1 that these compounds are formed at high temperatures, i.e. under conditions in which such a labile condition would be most unstable.

All these difficulties, as is obvious, are the necessary consequences of supposing that valency acts as an individual force. If this hypothesis be laid aside, then it is possible to obtain a satisfactory picture for poly-bound atoms. This will be described in a later chapter.

(γ) The Behaviour of Carbon Compounds containing several Ethylene Linkings.

Phenomena, irreconcilable with the supposition that valency is a directed individual force, are also to be observed in compounds which contain several double bonds. Compounds, in which both ethylene-linkings are contiguous, thus >C=C-C=C<, form addition compounds on the end atoms according to the equation:

Baeyer, when working on muconic acid, was the first to draw attention to this behaviour. Thiele 2 explains the unsaturated condition of the end carbon atoms by supposing there exists on the two middle carbon atoms a certain amount of residual affinity; this residual affinity being a necessary consequence of the formation of ethylene linkings. The middle carbons are therefore able, to a certain degree, to mutually saturate themselves, and the end carbons, being unable to do so, remain unsaturated and consequently in a position to form addition compounds. Thiele represents such a so-called conjugated system in the following way:

² Annalen, 306, 87 (1899).

¹ V. Meyer, "Ergebnisse und der Stereochemischen Forschung," Ber., 23, 582 (1890).

It is clear that such a division of valencies is impossible on the assumption that valency is an individual force.

(δ) The Conversion of Geometrical Isomers.

The limited rotation of doubly bound carbon atoms is explained by supposing that the valencies constituting the double bond are not parallel, but at an angle to one another. This supposition is the logical outcome of Van't Hoff's theory, in which the valencies are supposed to be at the corners of a regular tetrahedron. It is difficult, however, to reconcile this theory with the well-known transformation of geometrical isomers. A few examples of these transformations may serve to bring the subject freshly to mind.

The action of mineral acids, particularly halogen acids, cause maleic acid to be quantitatively transformed into fumaric acid. The same result is brought about by heating a 10 to 30 per cent. solution to 200-220°.2

The esters of maleic acid likewise are transformed into the esters of fumaric acid by halogen acids, and quantitatively by a trace of iodine.³ The opposite change also takes place; fumaric acid on distillation passes into maleic anhydride.

Crotonic acid on long heating at $160-180^{\circ}$ passes into isocrotonic acid, β -chlorerotonic on heating at 160° for twenty-four hours passes into β -chlorisocrotonic acid, δ etc.

The explanation of these phenomena proposed by Wislicenus,⁶ viz. the configuration most favourable to these changes is produced from the unfavourable by the formation of addition compounds, was unable to withstand an experimental test, and consequently is untenable.

Still more unnatural is that proposed 7 to explain the transformation of the two crotonic acids.

² Tanatar, Ber., 23, abs. 433 (1890).

' Fittig, ibid., 9, 1194 (1876).

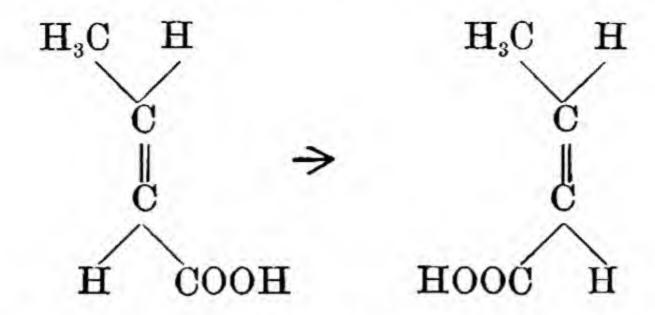
⁵ Friedrich, Annalen, 219, 370 (1883).

¹ Kekulé, Annalen, Supp., 1, 134; Annalen, 223, 186 (1883).

³ Osipoff, ibid., 12, 2095; Anschütz, ibid., 12, 2282 (1879).

[&]quot;Über die räumliche Anordnung der Atome in organischen Molekülen, p. 88.

Wislicenus, loc. cit., p. 55.



According to this explanation either an interchange of position occurs between the radicles united with the C: C group in order to produce a more stable compound, or the double bond between the carbon atoms is loosened so far, that by the action of the strong affinities a turning movement of the system follows, after which comes a wandering of a hydrogen atom to the nascent affinity of one of the radicles not causing this rotation, and finally, the reformation of the double bond takes place.

The necessity of making such complicated suppositions shows that the hypothesis which requires valency to be a force which acts solely in one definite direction leads to an untenable position. When it is further borne in mind that the hypothesis is likewise unable to explain the addition of reagents to ethylene compounds in the trans-position, we are forced to conclude that it is useless when applied to the ethylene compounds.

We see, therefore, that in the most varied branches of chemistry objections may be brought against the theory which supposes valency to be a directed individual force, so that from a chemical standpoint it is improbable.

4. On the Nature of Principal and Auxiliary Valencies. The Coincident Character of Principal and Auxiliary Valencies.

From the definitions already given of principal and auxiliary valencies we should be justified in assuming that these two types of valencies were quite different from one another. Such an assumption would be wrong, for many phenomena indicate that in their method of action both valencies are in many ways identical. This may be seen primarily from the fact that just those elements are bound by auxiliary valencies which form principal valency compounds either with particular ease or form particularly stable compounds. The following examples will illustrate this in a convincing way.

The salts of the alkalis and alkaline earths, the oxides of which

are characterized by their stability, form, through the addition of water or alcohol, well characterized hydrates and alcoholates. Those sulphides distinguished for stability yield addition products with alkaline sulphides, e.g. the salts of mercury, silver, and platinum, iron, chromium, arsenic, and antimony are well known for their ability to form sulpho salts. The halogen compounds of the platinum elements, which are noted for their stability, yield well-characterized and very stable halogeno salts, e.g. platinum chloride, gold chloride, paladium chloride, etc. Many analogous examples can be mentioned.

That principal and auxiliary valencies are closely related is to be seen further in the fact that the saturation of one will either strengthen or weaken the other. Thus, for example, higher oxides which are unstable in the free form become stable through salt formation. This is true for iron trioxide, which in its ferrates is stable; and also for the bromates and many persalts, which cannot as such be prepared in the free state, etc. A similar state of things is demonstrable for the higher halogen derivatives. In the free state it is impossible to prepare manganese tri- and tetrachloride, but in the form of double chlorides they are easily prepared; lead tetrachloride is likewise more stable in the form of its double chlorides. Trivalent cobalt, which in its ordinary salts is very unstable, becomes very stable on the addition of ammonia; this is also an example of the same class of pheno-That the principal valencies, on the other hand, can be weakened is to be seen in the ease with which carbon monoxidecuprosulphate (CuCO)SO, can be prepared, whereas cuprosulphate Cu2SO, can only be prepared with difficulty. Iron exhibits a similar phenomenon. While the salts of divalent iron are very unstable, and even pass into the trivalent condition by action of the air, the opposite reaction takes place when iron is combined with 3 molecules of α-dipyridyl or 3 molecules of σ-phenanthroline. Trivalent iron is, under these conditions, only to be retained by very cautious work; it passes with very great ease into the divalent condition.

Finally, that the auxiliary valencies, in like manner, can undergo a change dependent upon the groups used to saturate them is seen in the fact that different salts of the same element do not always unite with the same number of molecular compounds. Thus cadmium bromide and iodide unite with six molecules of pyridine, to form $[CdPy_6]Br_2$ and $[CdPy_6]I_2$, but the nitrate only takes up two molecules of pyridine. A similar behaviour is observed in the compounds manganese bromide and manganese nitrate. Copper bromide and copper chloride likewise combine with different quantities of pyridine, the former with six, and the latter with two molecules. Grossman in particular has drawn attention to such behaviour.

This close relationship between principal and auxiliary valencies permits the existence of a series of compounds, intermediate between both kinds of valency, to be predicted. In such a series it ought to be impossible to decide to which class of valency the component groups belong.

Two examples will suffice to illustrate this class, viz. sodium

nitroprusside and potassium carbonylferrocyanide-

$$\begin{bmatrix} \mathrm{Fe}^{\mathbf{NO}}_{\mathbf{C}\mathbf{y}_5} \end{bmatrix} \mathbf{Na_2}^2 \qquad \begin{bmatrix} \mathrm{Fe}^{\mathbf{CO}}_{\mathbf{C}\mathbf{y}_5} \end{bmatrix} \mathbf{K_3}^3$$

In these compounds it is practically impossible to decide to which class of valency the NO and CO groups belong, and it on this account appears doubtful whether it is permissible to ask this question in such cases.

Purely for structural formulæ, *i.e.* for the pictorial representation of the atomic linkings as deduced from the chemical properties of their compounds, the difference between principal and auxiliary valencies has little or no significance, and the most natural course to take is to make no difference between the bonds, but simply indicate their position by a point or line between two united atoms. Nevertheless it appears desirable to preserve for the present the difference between principal and auxiliary valencies, for to-day the doctrine of valency is in a transition state, and hence it is judicious to construct sharply defined conceptions, which will serve, at a later date, as the foundation stones of a comprehensive doctrine of valency. On this account, when a difference between principal and auxiliary valencies has to be made, the former may be indicated by a straight line and the latter by a dotted line.

¹ Ber., 37, 564, 1253 (1904).

² Playfair, Annalen, 74, 317 (1852); Kyd, ibid., p. 340 (1852); Hoffmann, ibid., 312, 1 (1900).

³ Müller, Compt. rend., 129, 962 (1899).

5. The Electrochemical Conception of the Principal Valencies.

(a) General.

When defining principal and auxiliary valencies we left unconsidered the fact that the former often confer ionogene properties on the radicles they bind, while those radicles which are linked by auxiliary valencies never appear as ions. This difference of property is characteristically shown when metallic atoms are attached by principal and secondary valencies to the same group, as, for example, in the "inner complex salts" (copper glycocoll, etc.). Such salts in aqueous solution exhibit no dissociation, while, when the same metal is bound by principal valencies to a completely analogous group (copper acetate), dissociation takes place. It is, nowadays, generally accepted that a definite quantity of electricity is associated, in the form of atoms of electricity (electrons), with such atoms; and that every unit of valency binds an electron (96540 coulombs). Lately the additional assumption has been introduced that in salts an electron (for every unit of valency) has been given up by the positive atom and been attached to the acid residue. From this standpoint, atoms which are bound together by principal valencies are characterized by the fact that this displacement of electrons can take place, a procedure which is impossible with auxiliary valencies.

The author at one time was of the opinion that this difference in behaviour was due to a fundamental difference between the two types of valency, but latterly has changed his opinion, and now believes that the electrochemical phenomena accompanying the saturation of principal valencies is a secondary action, and quite different from the purely chemical one. It may, however, accompany chemical change, but is not a necessary consequence. The electrochemical change is only dependent on the chemical in as far as the saturation of the affinity causes at the same time a loosening of the electron on the positive atom, and thus makes possible the transference of the electron to the negative component of the salt. It should be remembered, nevertheless, that the mere saturation of the principal valencies is insufficient to bring about this transference, for many binary compounds are unionized although the atoms are linked together by principal valencies. In such cases it is necessary that some auxiliary valencies be saturated before the ionization of SINGH COL these atoms is brought about. The number of auxiliary valencies

which have to be saturated first has already been defined as the "ionogene auxiliary valency number."

(b) The Difference between Ionogene and Non-ionogene Linkings.

The conception developed above, viz. that when principal valencies are saturated two changes take place, one purely chemical, and the other electrochemical, is of great importance to the theoretical treatment of the problem of valency. On the one hand, it offers a basis upon which it is possible to reconcile the doctrines of principal and auxiliary valencies, which up to the present have been irreconcilable, and, on the other hand, the theory leads to conclusions which tend to clear up a series of phenomena which have up to the present been incomprehensible. These may be set forth in what follows. To explain the difference between ionogene and nonionogene groups two suppositions may be made, either that the electrochemical change, i.e. the transference of an electron, takes place simultaneously with the saturation of the auxiliary valencies, or that such a transference is only possible in solution. This latter supposition appears to the author to be the more improbable one because it is possible to prove differences between ionogene and non-ionogene groups even when the compounds are not in solution but in the solid state. For example, on pouring concentrated sulphuric acid over solid cobaltates ionogene chlorine is immediately evolved as hydrochloric acid, but the non-ionogene chlorine remains unaffected. Our first supposition, however, leads to the important conclusion that principal valencies can produce two different kinds of linkings, viz. the non-ionogene bonds, in which electronic-transference has not taken place, and ionogene bonds, in which such a transference has been completed. This difference may be represented schematically as follows:

Me[©]—X Me—X[©] ionogene bond

The conclusion that the two types of principal valencies exist partly covers Baeyer's theory. The essential difference between the two theories rests in the idea that the principal valencies undergo a change when the auxiliary valencies on the atom are saturated. Consequently, our theory, in opposition to Baeyer's, does not predict the existence of the isomers Me 1—X and Me—X.

¹ The abbreviation Me has been used to represent the word "metal"; M to represent "metalloid."

Our representation touches upon the complicated conception of Abegg and Bodländer on the strengthening of the electro-affinity of simple ions through the formation of complexes, for the molecules which we suppose joined by auxiliary valencies correspond to the so-called neutral parts of Abegg and Bodländer.

In certain cases a change of colour is observed in a compound in which a non-ionogene principal valency changes into an ionogene linking; this phenomenon has been called by Baeyer "Halochromism." This is very well exhibited in the colourless triphenyl chlormethane, which becomes yellow on the addition of metallic halides to the chlorine, e.g. $(C_6H_5)_3C$. Cl. SnCl₄, etc. Colourless phenolphthalein becomes an intense red on the addition of AlCl₃ and SnCl₄, and yields salts of the formulæ $C_{20}H_{14}O_4$. AlCl₃ and $C_{20}H_{14}O_4$. SnCl₄. It is not always possible to decide whether a change of constitution accompanies the transition of an non-ionogene into an ionogene compound. In some instances this is the case, but whether it is invariably so is doubtful.

6. The Affinity Value of Valencies.

(a) The Variable Affinity Values of Principal Valencies.

The previous paragraph has proved that principal and auxiliary valencies are identical, and it could be shown that units of valency cannot be considered as definite individual forces. In conclusion we have only to decide how the unit of valency is to be defined. According to my idea the complicated doctrines of valency and co-ordination can only be viewed from a common standpoint, when it is assumed that the unit of valency is not constant, but varies with the nature of the atoms it joins together, and with the variable amount of affinity on these atoms. This assumption lends itself to experimental test. For example, if the affinity content of the atom Me in the system Me-X, becomes saturated owing to Me being linked to other atoms and groups, then Me has less affinity over than it had previously for the bond between Me and X, with the result that X has a certain amount of residual affinity. Should this reach a certain value, it will be able to produce auxiliary valencies, and hence the formation of molecular compounds will be In such cases addition compounds MeX. A are to be expected. They are to be expected particularly in the compounds

¹ Meyer and Hantzsch, Ber., 40, 3479 (1907).

MeXn in which n, the limiting number of the principal valencies, has been reached. In such compounds it is probable that the nth valency will be weaker than the others, and hence the radicle bound by it will be able to form addition compounds. These theoretical considerations have been fully confirmed by experiment.

Thus, in the limiting compounds of the halides, one halogen atom has exhibited a capacity for the exercising of an auxiliary valency. This power is evinced by the inclination displayed by halides for the formation of halogen salts. The following compounds evince this tendency: SCl₄, SeCl₄, PCl₅, PBr₅, etc., for they form salts like potassium chloride:

$$KCl + AuCl_3 = K(Cl_4Au)$$

 $Cl_3SCl + AuCl_3 = Cl_3S(Cl_4Au)$
 $Cl_3SeCl + AuCl_3 = Cl_3Se(Cl_4Au)$
 $Cl_4PCl + AuCl_3 = Cl_4P(Cl_4Au)$

The following examples illustrate this class of salts:-

- 1. SCl₄: Cl₃SCl. AuCl₃,¹ Cl₃SCl. FeCl₃,² Cl₃SCl. SbCl₅,³ Cl₃SCl. AlCl₃,⁴ (Cl₃SCl)₂SnCl₄,⁵ (Cl₃SCl)₂TiCl₄.⁶
- 2. SeCl₄: Cl₃SeCl. AuCl₃,⁷ Cl₃SeCl. SbCl₅.⁸
- 3. PCl₅: Cl₄PCl. AuCl₃,⁹ Cl₄PCl. AlCl₃,¹⁰ Cl₄PCl. MoCl₄,¹¹ Cl₄PCl. UCl₅,¹² Cl₄PCl. SnCl₄,¹³ Cl₄PCl. TiCl₄,¹⁴ Cl₄PCl. SbCl₅,¹⁵ Cl₄PCl. ICl,¹⁶ Cl₄PCl. CrCl₃,¹⁷
- ¹ Lindet, Compt. rend., 101, 1492 (1885).
- ² Ruff and Einbeck, Ber., 36, 418 (1903).
- ³ Ruff and Fisher, ibid., 36, 418 (1903).
- ⁴ Ruff and Plato, ibid., 34, 1749 (1901).
- ⁵ Rose, Jahresber., 1852, 393; Pogg. Ann., 42, 517 (1837).
- 6 Rose, Pogg. Ann., 15, 145; 16, 57; 42, 517 (1837).
- ⁷ Lindet, Compt. rend., 101, 1492 (1885).
- ⁸ Weber, Pogg. Ann., 125, 78 (1865).
- ⁹ Lindet, Compt. rend., 101, 164 (1885).
- 10 Weber, J. pr. Chem., (1) 76, 408; Baudrimont, ibid., (1) 88, 80 (1863).
- ¹¹ Cronander, Bull. Soc. Chim., (2) 19, 500 (1873).
- ¹² Ibid. ¹³ Casselmann, Jahresber., 1852, 394.
- 14 Weber, ibid., 1867, 206; Pogg. Ann., 132, 452 (1867).
- · 15 Weber, ibid., 125, 178; Cronander, Bull. Soc. Chim., (2) 19, 499 (1873).
 - 16 Baudrimont, Compt. rend., 55, 361 (1862).
 - 17 Cronander, Bull. Soc. Chim., (2) 19, 501 (1873).

¹ A. Werner, "Über den wechselnden Affinitätswert einfacher Bindungen," Ber., 39, 1278 (1906).

4. PBr₅: Br₄PBr . AuBr₆, Br₄PBr . BBr₃, Br₄PBr . Br₂.

- ¹ Cronander, Bull. Soc. Chim., (2) 19, 501 (1873).
- ² Baudrimont, Compt. rend., 55, 361 (1862).
- ³ Cronander, Bull. Soc. Chim., (2) 19, 500 (1873).
- 4 Baudrimont, Compt. rend., 55, 361 (1862).
- ⁵ Lindet, ibid., 101, 164 (1885). ⁶ Carible, ibid., 116, 1521 (1893).
- ⁷ Kastle and Beatty, Amer. Chem. J., 21, 392 (1899).

In organic compounds similar phenomena are to be observed particularly in the triphenylmethane series. Triphenylchlor-methane, and its homologues, form the following class of compounds:

$$\begin{array}{ll} (C_6H_5)_3CCl \ . \ AlCl_3^{\ 1} & (C_6H_5)_3 \ . \ C\ Cl \ . \ SnCl_4^{\ 2} \\ 2(C_6H_5)_3C\ Cl \ . \ (HgCl_2)_3^{\ 3} & 2(C_6H_5)_3C\ Br \ . \ (HgBr_2)_3^{\ 3} \\ (C_6H_5)_3C\ Cl \ . \ ZnCl_2^{\ 3} & (C_6H_4 \ . \ CH_3)_3CCl \ . \ HgCl_2^{\ 3} \\ & (C_6H_4 \ . \ CH_3)_3CCl \ . \ HgCl_2^{\ 3} \end{array}$$

- ¹ Norris and Sanders, Amer. Chem. J., 25, 54 (1901).
- ² Kehrmann, Ber., 34, 3818 (1901).
- ³ Gomberg, J. Amer. Chem. Soc., 23, 496 (1901).

This leads us to suppose that the affinity of the carbinol carbon has great claims laid upon it by the three phenyl groups, which results in a very small residue remaining for the fourth radicle. This latter radicle is therefore unsaturated, and is consequently able to form addition compounds.

Our discussion therefore leads us to conclude that the valencies of the elements in their compounds, although they are all indicated in structural formulæ, in the same way, i.e. by a stroke, are not all of the same value.

(b) Differences between the Affinity Value of Principal and Auxiliary Valencies.

Atoms whose affinity content is already to a great extent saturated, will have a smaller amount of affinity remaining than those in which this is not the case. Thus, the oxygen atom in water has less unsaturated affinity than the hydroxyl group. This remark can be made of general application by saying that the elementary atoms of complex molecules have less affinity for the formation of molecular complexes than the atoms of radicles. We must conclude, since in the former chiefly auxiliary valencies

are active, and in the latter principal valencies, that the saturation of auxiliary valencies usually requires a less amount of affinity than that required by principal valencies. There is, therefore, a gradual difference in the affinity values between principal and auxiliary valencies. So that we should expect all possible values in a transition series between both types of valency, and it would consequently be impossible to fix sharp limits between them—an inference completely borne out by experiment.

(c) The Affinity Value of "Incomplete Bonds."

On comparing ethylene compounds with other compounds, we see that the degree of saturation of the ethylene carbon atoms assumes a sort of intermediate position between the carbon atoms in the paraffins and the carbinol carbon in triphenyl methyl, and according to the nature of the atoms in combination with the ethylene carbons either of these stages of saturation is reached. We can, therefore, distinguish different degrees of saturation in ethylene carbon atoms. They are usually more saturated than carbinol carbon in triphenylmethyl, and in some cases they are so strongly saturated, that they do not exhibit some of the characteristic reactions of ethylene carbons, e.g. the addition of bromine to tetraphenylethylene. In other cases their highly unsaturated character may be distinctly recognized in certain phenomena, e.g. the tendency for polymerization exhibited by certain ethylene bodies, particularly those which polymerize merely through the action of light, as cinnamic acid, styrol, cumarin, etc. Finally, there are ethylene compounds known, which scarcely differ in their degree of saturation from triphenylmethyl, thus dimethyl fulvene, which has been examined by Engler and Frankenstein,1 passes into a disuperoxide, C₈H₁₀O₄, through the absorption of atmospheric oxygen. Some other fulvenes under like conditions also yield superoxides.

Amongst the terpines there are also some ethylene compounds (pinenes) which absorb atmospheric oxygen and pass into super-oxides.

From such varied behaviour we draw the conclusion that polybound atoms exhibit a degree of saturation the value of which is dependent on the nature of the atoms to which they are joined.

This is smaller than that expressed in the structural formula, but greater than the next lower degree of saturation as expressed by valency formula.

IV. Concluding Considerations on Affinity and Valency.

The proof that the affinity value of atomic bonds is variable, naturally leads to the idea that the phenomena contained in the doctrines of valency and of co-ordination can be developed from certain fundamental suppositions on affinity. As a matter of fact, this can be shown to be true without making any improbable assumptions.¹

Let us suppose that the atom consists of homogeneous matter. Hypotheses on the form of the atom are unnecessary, because the atom, both free and in a molecule, must be supposed to be always in motion, and its particular form with respect to its spacial limits within which it oscillates can only be of secondary importance. But for the sake of simplicity we can suppose it to be a sphere, and further, such a supposition also simplifies our mechanical picture of the structure of the molecule.

We will also make the following simple suppositions on affinity. Affinity is an attractive force which acts from the centre of the atom, and is of equal value at all points on its surface. With such a definition of affinity it naturally follows that separate units of affinity do not exist. Valency is a numerical ratio which has been empirically found, is independent of units, and expresses the ratio in which atoms combine with one another. It does not depend upon one atom alone, but rather upon the nature of all the atoms present in a particular molecule. The amount of affinity saturated by the linking up of two atoms is distributed on a definite circular segment on the surface of the atom (binding zone), and varies within wide limits with the nature of these atoms.

We have in these assumptions a satisfactory picture of the varying valency ratios of an elementary atom, which leads, without any further assumptions, to the spacial configuration of the molecule, the shape of which depends only on the size of the binding zone. I have already shown in another place 2 that it is possible with

² Loc. cit. and in my Lehrbuch der Stereochemie, Jena, 1904.

¹ Werner, "Beiträge zur Theorie der Affinität und Valenz," Vierteljahrsschr. d. Züricher naturforsch. Gesellsch. (1891).

such an hypothesis to explain in a simple manner the phenomenon of racemization, the transposition of geometrical isomers, and the stability of ring compounds. Bloch has shown how closely the inferences we have made from our hypotheses agree with the observations made in the most varied branches of organic chemistry.

B. Systematic Division.

I. Compounds of the First Order.

1. Introduction.

A chemical molecule in its simplest form, excepting elementary molecules, is produced when two different atoms unite. Compounds of this simple description we call "binary compounds" or compounds of the first order. Examples of this class are: NaCl, KF, CaO, ZnS.

In order to avoid any misapprehension, it may be mentioned that only compounds of the above type come within the definition. All combinations of these compounds with water, ammonia, etc., are not compounds of the first order, but of higher order, and lie outside the present discussion.

2. Nomenclature.

By common agreement compounds of the first order have the termination ide at the end of the negative element, e.g. sodium chloride, zinc sulphide, etc. The general use of this nomenclature would be so great a boon to inorganic chemistry that great care ought to be exercised to prevent the adoption of such terms as hydride, carbide, etc., which can only be harmful to the clearness of the system. And it is greatly to be desired that the nomenclature should be further developed. This could be done by placing before the name of a negative element the number of times the latter is contained in the molecule, e.g. CuCl, copper monochloride; FeCl₂, iron dichloride; FeCl3, iron trichloride; PtCl4, platinum tetrachloride; FeO, ironmonoxide, etc. Such an addition to the names would be of great advantage to the memory, for when using such names as ferrochloride, cuprochloride, ferrichloride, platinichloride, etc., we have to remember not only the names but also the valencies of the metal in compound.

¹ E. Bloch, A. Werner's Theorie des Kohlenstoffatoms, Wien u. Leipzig, 1903.

It would be even more simple if all those compounds of the same valency had their names ending in the same letter or suffix, thus:—

MeX				a-Co	ompound (monovalent)				
MeX_2				0-	,,	(divalent)			
MeX ₃				i-	"	(trivalent)			
MeX,	,			e-	11	(tetravalent)			
MeX,				an-	"	(pentavalent)			
MeX,				on-	"	(hexavalent)			
MeX,				in-	**	(heptavalent)			
MeX_8	٠			en-	**	(octavalent)			

This suggested nomenclature I communicated to Brauner several years ago, and he has called attention to it in a paper of his.¹

In the mean time it has been used by different authors,² and it is to be hoped that it will find increasing use.

The suffixes have been chosen with a view to making them as little different as possible from those already in existence. The use of this nomenclature will only cause confusion in mercury and copper salts. The monovalent compounds, which at present are termed mercuro- and cupro-salts, would become mercura- and cupra-salts; while mercuri- and cupri-salts would become mercuro- and cupro-salts. This is, of course, a disadvantage, but it is trifling when compared to the great benefits to be obtained from the use of this nomenclature.

However, in order to completely exclude any possibility of confusion, I suggest that "n" be written after divalent copper and mercury compounds, to signify that it is the "new nomenclature" that is being used, e.g. HgCl₂, mercurochloride (n); CuBr₂, cuprobromide (n).

To illustrate the use of the suggested nomenclature the different salts of vanadium and molybdenum are given:

VX2.	•			Vanad-o-salts.	MoX.			Molybd-o-salts.
VX ₃ .	•	÷						Molybd-i-salts.
								Molybd-e-salts.
VX,				Vanad-an-salts.	MoXs .			Molybd-an-salts.
								Molybd-on-salts.

¹ Zeitsch. anorg. Chem., 32, 10 (1902).

² Groth, Einleitung in die chemische Kristallographie (1904); Gemelin-Krauts Handb. d. anorg. Chem., 7th edition (1908); Cobaltates, by P. Pfeiffer.

When the names of the compounds are long it is advantageous to accent the suffix which expresses the valency, e.g. magnesium-ō-salts, etc.

3. Systematics.

The systematics of inorganic chemistry finds its expression in the nomenclature developed above, because the nature of the negative element is the more important part of the molecule. Compounds of the first order may consequently be classed under such groups as the following: Fluorides, chlorides, oxides, senenides, phosphides, antimonides, carbides, borides, etc.

Certain compounds of the first order can, if composed of the same elementary atoms, possess a complex constitution, thus carbides of hydrogen:

the superoxides:

$$\begin{array}{ccc}
\mathbf{Ba} & \mathbf{H} & \mathbf{H} & \mathbf{0} \\
\mathbf{Ba} & \mathbf{H} & \mathbf{0}
\end{array}$$

and other compounds such as cyanogen:

The complicated constitution of such compounds makes a uniform nomenclature more difficult, but, since the character of the compound is unaffected by the linkings between two atomic groups of the same description, it leaves their position in the system unaffected.

Therefore it is advisable to designate the compounds H₃C—CH₃

To be sure, if it were desired to be absolutely logical, H₃C—CH₃ could be considered as a mixed carbide of carbon and hydrogen, and the compound Ba as an oxide of barium and oxygen, etc. This would be of no advantage to the systematics, but is rather detrimental to its lucidity.

and
$$H_3C$$
— CH_2 — CH_3 as hydrogen carbides, HO as oxide of HO

description can be considered as being derived from those of the first order. Further, those compounds whose molecular constitution is the same as the binary compounds, can be included in the compounds of the first order, although they consist of more than two elements, as, for example:

As a matter of fact, such compounds form a sort of transition stage between those of the first and those of the higher order.

A systematic consideration of the individual groups of the first order would take up too much space. We must therefore be satisfied by briefly indicating those groups, the examination of which, within recent years, has so greatly extended our knowledge on the combining possibilities of the elements.

The hydrides deserve first mention. They are binary compounds in which hydrogen is the negative element, which, on the whole, plays the same rôle as the halogens in halides. It is to Moissan that we chiefly owe our thanks for our knowledge of this group.

A great increase in our knowledge of the combining possibilities of the elements has been made through the study of the fluorides, to which class of compounds O. Ruff has lately so successfully given his attention. The following types serve to illustrate the class: IF₅, SF₆, SeF₆, TeF₆, NF₅, WOF₄, MoF₆, MoOF₄, MoO₂F₂, etc.

Other binary compounds, the study of which has added to our knowledge of the combining possibilities of the elements and in part has completely altered our ideas, are the carbides, silicides, and borides.

Valuable results have also been obtained from the study of alloys. Tammann and his pupils, through thermal analysis, Kurnakow and many other experimenters have so enriched our knowledge of the chemical properties of metallic alloys, that for

the first time it seems possible to obtain an idea of how metals combine with one another. Tammann, for example, has pointed out that those metallic elements which succeed one another in the periodic system are usually unable to combine with one another. This is true, for example, in the following groups: Cu, Ag, Au; Zn, Cd, Hg; Ge, Sn, Pb; As, Sb, Bi. Cobalt forms a compound with neither nickel nor iron; on the other hand, nickel forms the compound Ni₂Fe. He has shown, further, that in many cases either all three of the homologous metals potassium, rubidium, and cæsium form compounds with another definite element, or not one of them does so.

II. Compounds of Higher Order

1. Halogeno Salts and Analogous Compounds.

Compounds of higher order, which are produced by the union of simple halides, are usually called double halides, and since most simple halides have the character of salts (halide salts) they are mostly called double salts. It is more suitable to use the term "halogeno salts" in order to bring out their analogy to the oxygen salts. In number and importance the halogeno salts are quite equal to the oxygen salts; indeed, in some elements, e.g. the noble metals, they play a more important part than the oxygen compounds.

(a) Properties of the Halogeno Salts.

Just as acid and basic forming oxides are chemically opposed to one another, and through their union form oxygen salts, so fluorides, chlorides, etc., exhibit towards different elements a difference in their chemical character which, if not the cause of their forming complex compounds, at any rate greatly increases it.

Some examples will illustrate the type of compound under discussion:

$$F_3B + FR = BF_4R$$

 $Cl_4Pt + 2ClR = PtCl_6R_2$
 $Br_3Sb + 3BrR = SbR_6R_3$
 $I_3Ir + 3IR = IrI_6R_3$

In all these cases we can show that a halide of an electropositive radicle combines with a halide of a less positive element (heavy

¹ Zeitsch. anorg. Chem., 49, 113.

metal or metaloid). If we call the former compound, which plays in this case the same rôle as the basic oxide, a basic halide, the latter may be called an acid halide.

In the halogeno salts the central atoms of the acid-forming halides combine with the halogens of the basic halides to form complex radicles, which can appear as complex acid ions on electrolytic dissociation. In the above examples the following groups exercise this function:

A further analogy between oxygen and halogeno salts is to be found in their behaviour towards water. While, as is well known, neutral salts in aqueous solution are electrolytically dissociated, and basic salts are hydrolytically dissociated:

$$CO_{^3}H^{^3} + H_2O = CO_3H_2 + NaOH$$

Exactly analogous phenomena are to be observed in halogeno salts. Some—e.g. the alkali chloroplateates—dissociate in aqueous solutions into ions:

while others are decomposed by water, the basic chloride being replaced by water, e.g.:

[CuCl₃] K + H₂O = Cu
$$_{(OH_2)}^{Cl_2}$$
 + KCl

Other properties in which halogen salts closely resemble oxygen salts will be made clear in the following paragraphs.

(b) Nomenclature of the Halogeno Salts.

The nomenclature of the oxygen salts is well worked out, since the oxygen salts have themselves been thoroughly examined, but this is not true of the nomenclature of the halogeno salts, and their analogous compounds. I believe a satisfactory nomenclature can be obtained upon the following basis:—

- 1. In order to differentiate between the double and the simple halides it is advisable to use at the end of their names the suffix "ate," a term already in use in the oxides.
- 2. The valency of the central acid radicle is to be expressed in exactly the same way as was used with compounds of the first order.

3. The name of the acid residues bound to the central atom will be placed before the name of this atom.

The following names illustrate the practical application of these rules:

- 1. (AgCl₃)Cs ¹ . . . Cæsium-Trichloroargentaate.
- 2. (ZnCl₅)(NH₄)₃² . . Ammonium-Pentachlorozinciate.
- 3. (FeCy₆)Na₃ ³ . . . Sodium-Hexacyanoferriate.
- 4. $(MnF_6)K_2^4$. . . Potassium-Hexafluoromanganoate.
- 5. (SbCl₆)Cs ⁵ . . . Cæsium-Hexachlorostibanate.
- 6. $\left[\mathbf{U}_{\mathrm{Br_{4}}}^{\mathrm{O_{2}}}\right]$ $\mathbb{K}_{2}^{\mathrm{6}}$ Potassium-Dioxotetrabromouranonate.
 - 1 Wells, Sill., (3) 44, 221, 311 (1892).
 - ² Marignac, Ann. Min., (5) 12, 1 (1857); Jahresber., 1857, 218.
 - ³ Bette, Annalen, 23, 124 (1837).
 - ⁴ Weinland and Lauenstein, Zeitsch. anorg. Chem., 20, 40 (1899).
- ⁵ Wells and Metzger, Amer. J. Sci., (4) 11, 451; Chem. Centr., 2, 166 (1901).
 - 6 Sendtner, Verbdg. d. Urans. Elangan, 1877.

(c) Constitution of Halogeno Salts.

Following the example of Blomstrand onstitutional formulæ of the following description were originally proposed for the double halides:

and for those compounds in which the sum of the halogen atoms in the basic halides is greater than that in the acidic halides, Remsen,² suggested the following constitutions:

All these formulæ are only of historical interest nowadays, for it will be remembered that, taking chloroplatinic acid as illustration, it was shown in the general part of this book that in all these double halides the halogen atoms of the basic halide are bound to the

- 1 Die Chemi der Jetztzeit, p. 333. Heidelberg, 1869.
- ² Amer. Chem. J., 11, 291 (1899); ibid., 14, 81 (1892).

central atom, which acts as an acid anhydride. The compounds cited above must therefore have their constitution expressed by the formulæ:

$$\begin{bmatrix} \mathbf{F} \\ \mathbf{F} \end{bmatrix} \mathbf{R} \quad \begin{bmatrix} \mathbf{Cl} \\ \mathbf{Cl} \\ \mathbf{Cl} \end{bmatrix} \mathbf{Pt} \cdot \begin{bmatrix} \mathbf{Cl} \\ \mathbf{Cl} \\ \mathbf{Cl} \end{bmatrix} \mathbf{R}_{2} \quad \begin{bmatrix} \mathbf{Cl} \cdot \mathbf{Cu} \\ \mathbf{Cl} \cdot \mathbf{Cu} \\ \mathbf{Cl} \end{bmatrix} \mathbf{R}_{2} \quad \begin{bmatrix} \mathbf{Cl} \cdot \mathbf{Cd} \\ \mathbf{Cl} \cdot \mathbf{Cd} \\ \mathbf{Cl} \end{bmatrix} \mathbf{R}_{4}$$

It follows, consequently, that the halogen atoms act as connecting links between two elementary atoms, and therefore in pure structural relations are to be considered as divalent.

The new constitutional formulæ differ from those which were earlier proposed, chiefly in the fact that in them not double halogen atoms but single atoms play the same part as an atom of oxygen in oxygen salts.

The constitutional analogy between halogen salts and oxygen salts may be expressed by writing their formulæ analogously, as in the chloroauriates and sulphates:

$$\begin{array}{cccc} \text{Cl} & & \text{O} \\ \text{ClAuClR} & \text{and} & \text{OSOR}_2 \\ \text{Cl} & & \text{O} \end{array}$$

The great advantage of these formulæ rests in the fact that they bring out this analogy much more clearly than was possible by the old doctrine of valency.

With reference to the problem of the constitution of halogeno salts two points remain to be decided: (a) the establishment of their molecular weight and that of the halide which acts as acid anhydride; and (b) the determination of the functions or of the position of the water in a hydrated halogeno salt, for in both these directions the experimental material is very deficient.

(d) On the Forms of the Halogeno Salts derived from the same Halogeno Acid Anhydride.

As is well known, different hydrates (acids) and salts may be derived from the same acidic anhydride of an oxide. Thus, phosphorus pentoxide gives rise through the absorption of one, two, or three molecules of water to three different acids (or salts, depending upon experimental conditions). The halogeno salts exhibit a similar behaviour, the fluorides less so than the others. Cadmium chloride can take up one, two, or four, zinc chloride one, two, or three, and

platinum chloride one or two molecules of alkali chloride. The other halides, which likewise act as acidic anhydrides, behave in an exactly analogous way. Thus from the same halogeno acidic anhydride different halogeno acids or salts may be obtained; their behaviour is therefore in complete agreement with that of the oxygen compounds. It is further worthy of note that the halides of the most positive metals, i.e. rubidium and cæsium, give rise to the salts of the highest form; this is again completely analogous to what is observed in the formation of oxygen salts. If we examine the stoichiometrical proportions in which the halides combine to form halogeno salts, it is seen that, with very few exceptions which will occupy our attention later, the upper limit is reached when six halogen atoms have taken part in the formation of a complete radicle. This is clearly seen from the composition of the salts of the divalent elements: cadmium and lead; of the trivalent elements: thallium, chromium, iron, iridium, osmium, rhodium, and almost all the tetravalent elements.

So that also in these cases the number six appears to be a stoichiometrical limiting number, which controls the formation of compounds of higher order.

(e) On the Polymeric Condition of Binary Halides.

It is well known that many halides are not monomolecular but polymolecular. Thus, iron chloride in the form of vapour corresponds to the formula (FeCl₃)₂, and under like conditions molybdochloride is trimolar (MoCl₂)₃.

In some cases the addition products formed by the halides are likewise polymeric, from which it is to be concluded that the halides themselves are polymeric. This is true, for example, of the product formed by the addition of a molecule of PCl₃ to PtCl₂, which is known to have the formula (PtCl₂. PCl₃)₂, and we conclude that platinous chloride is bimolecular.

In aqueous solution cadmium, zinc, and mercury halides are partly polymerized, and in organic solvents the same is true of copper and silver halides. Moreover, different halides of the alkali metals show a tendency to polymerization in ethyl alcohol, normal propyl alcohol and amyl alcohol, and in acetic acid they have a doubled molar weight.

¹ Rosenheim and Löwenstamm, Zeitsch. anorg. Chem., 37, 394 (1904).

Hydrochloric acid itself is bimolar in formic acid. Very many halides exhibit complex molecules in sulphur dioxide solutions. 1

These facts lead to the conclusion that halides, in general, possess the property of polymerization, and the question is, How is the formation of polymeric molecules to be portrayed? The following considerations yield a satisfactory explanation.

With some elements it is possible to show that their binary halides of different valency have the property to combine with one another, thus forming halogeno salts. Cases of this description have been satisfactorily investigated for salts of iron and thallium.

$$\begin{split} &\text{TlCl}_3 \,.\, 3\text{TlCl},^1 \quad \text{TlBr}_3 \,.\, \text{TlBr},^2 \quad \text{TlBr}_3 \,.\, 3\text{TlBr},^3 \quad [\text{Tl}(\text{ClBr})_4]\text{Tl},^3 \\ &[\text{Tl}(\text{ClBr})_6]\text{Tl}_3,^3 \quad \text{TlBr}_3 \,.\, 3\text{TlCl},^4 \quad \text{Tl}_{\text{Br}_2}^{\text{Cl}} \,.\, 3\text{TlCl},^4 \quad \text{TlCl}_3 \,.\, 3\text{BrTl},^4 \\ &\text{TlI}_3 \,.\, 5\text{TlI},^5 \\ &\text{FeBr}_2 \,.\, 2\text{FeBr}_3 \,.\, \text{KBr} \,+\, 3\text{H}_2\text{O},^6 \quad \text{FeBr}_2 \,.\, 2\text{FeBr}_3 \,.\, \text{RbBr} \,+\, 3\text{H}_2\text{O},^6 \\ &\text{FeCl}_2 \,.\, 2\text{FeCl}_3 \,+\, 18\text{H}_2\text{O},^7 \\ &\text{FeF}_3 \,.\, \text{FeF}_2 \,+\, 7\text{H}_2\text{O},^8 \, \left[\text{Fe}_{\text{F}_4}^{(\text{OH}_2)_2}\right]_2 \, [\text{Fe}(\text{OH}_2)_6].^9 \end{split}$$

¹ Neumann, Annalen, 244, 347 (1887).

² Wilm, Bull. Soc. Chim., (2) 2, 89 (1864).

³ Meyer, Zeitsch. anorg. Chem., 24, 353 (1900).

' Cushman, Amer. Chem. J., 24, 222 (1900).

⁵ Knösel, Ber., 7, 576, 893 (1874); Jörgensen, J. pr. Chem., (2) 6, 83 (1872).

Walden, Zeitsch. anorg. Chem., 7, 337 (1894).
 Lefort, J. Pharmac., (4) 10, 85; J., 1869, 267.

" Weiland and Köppen, Zeitsch. anorg. Chem., 22, 266 (1899).

Deussen, Monat. Chem., 28, 163 (1907).

The composition and character of these compounds distinctly show that they are produced in exactly the same way as other halogeno salts; thus, for example, TlBr₃ + 3BrTl according to the formula:

Br. BrTl
Br. BrTl
Br. BrTl

But if halides of the same element but of different valency can unite together to form halogeno salts, it is quite to be expected that molecules of the same halide should combine together, as, for example, iron chloride, according to the formula:

¹ For compilation of the literature see Walden and Centnerszwer, Zeitsch. physikal Chem., 39, 587 (1902).

Cl . Cl ClFe Cl . Cl

and thus bimolar ferric chloride is to be considered as the ferric salt of hexachloro-ferric acid. The polymerization of halides is consequently due to the formation of halogeno salts from the same kind of molecules, and the polymeric halides can therefore be called "auto-halogeno salts."

This theory renders it possible to lay aside the numerous hypotheses which have been proposed to explain the polymerization of halides, all of which assume linkings either between the metallic atoms or the halogen atoms, and they are moreover so different from one another that a reconciliation is impossible. Yet it should be noted that the question of the polymerization of the halides has only been solved as far as the principle is concerned; it is at present impossible to say anything further as to the exact constitution of polymeric halides. For there still remains several possibilities for the combination of the different halide molecules; thus, in the case of trivalent elements the following formulæ are possible:

which of these constitutional formulæ in each individual case is the more probable cannot at present be decided.

(f) On Polynuclear Halogeno Salts.

Polymeric halides can act as anhydrides of halogeno salts, and certain elements have an exceptionally great tendency to form halogeno salts with polymeric halides; thus mercury chloride yields compounds of the following types: Hg₂Cl₅R, Hg₃Cl₈R₂, Hg₅Cl₁₁R, etc.

Very interesting is the behaviour of the trimolar molybdo chloride (MoCl₂)₃; Blomstrand gave this compound the name chloromolybdane chloride. Of its six chlorine atoms, on treatment with alkali two are replaced by hydroxyl, and it therefore appears probable that the four less reactive chlorine atoms are integral parts of the molecular complex, while the two reactive ones have no part in its formation. Chloromolybdane chloride can act as the anhydride of a chloro acid, for it is able to combine with two

molecules of alkali-chloride, thus forming a salt with the formula (Mo₃Cl₈)R₂.

From the bimolar trihalides $(SbX_3)_2$, $(BiX_3)_2$, $(AsX_3)_2$, the following types of salts may be prepared: $(RX_3)_2$. XMe and $(RX_3)_2$. 3XMe. At first sight it would appear as if the intermediate salt $(RX_3)_2$. 2XMe did not exist; but this is incorrect, for it is usually formulated RX_3 . XMe.

Many examples of this type of compound are known, e.g.:

(SbCl₄)Rb, (SbCl₄)H.Chin, (BiCl₄)[Sb(C₂H₅)₄], (BiCl₄)Rb + H₂O, (BiCl₄)NH₄,

 $(BiBr_4)NH_4 + H_2O_5 (AsI_4)[As(C_2H_5)_4], (AsI_4)[(C_3H_7)_4As], (SbI_4)K.$ $(BiI_4)K, (BiI_4)NH_4 + H_2O.$

If we double the formulæ of these compounds, we obtain the following normal series:

$$(RX_3)_2$$
. XMe, $(RX_3)_2$. 2XMe, $(RX_3)_2$. 3XMe

Such considerations show how important it is to find methods for the determination of the molar weight of the halogeno salts. Then, and then only, will it be possible to obtain a satisfactory constitution for such salts.

(g) Polyhalides.

The alkalis and alkaline earths, as well as a few other elements and complex radicles with properties similar to ammonia, form polyhalides, *i.e.* compounds the positive radicle of which consists of several halogen atoms. The following list will give some idea of this class of compounds:

1. Trihalides.1

K(ICl₂), K(IBr₂), KI₃, Rb(BrCl₂), Rb(Br₂Cl), RbBr₃, Rb(ICl₂), Rb(IBrCl), Rb(IBr₂), RI₃, Cs(BrCl₂), CsBr₃, Cs(ICl₂), Cs(IBrCl), Cs(IBr₂), Cs(I₂Br), CsI₃, (NH₄)I₃, (PCl₄)(ICl₂), (PBr₄), Br₃,

$$\operatorname{Zn}_{\operatorname{I}_3}^{\operatorname{I}}$$
, $\operatorname{Hg}(\operatorname{I}_3)_2$.

Wells and Wheeler, Amer. J. Sci., (3) 43, 475 (1892); Wells, Zeitsch. anorg. Chem., 1, 85 (1892).

2. Pentahalides.1

 $Li(ICl_4) + 4H_2O$, $Na(ICl_4)$, $K(ICl_4)$, $Rb(ICl_4)$, $Cs(ICl_4)$, $Ca(ICl_4)_2 + 8H_2O$, $Sr(ICl_4)_2 + 8H_2O$,

 $Mg(ICl_4)_2 + 8H_2O$, $Be(ICl_4)_2 + 8H_2O$, $Zn(ICl_4)_2 + 8H_2O$, $Mn(ICl_4)_2 + 8H_2O$, $Co(ICl_5)_2 + 8H_2O$, $Ni(ICl_4)_2 + 8H_2O$, Csl_5 , Csl_5 .

Beyond these there still exist a great many polyhalide salts of organic compounds. Those of the diazonium group are particularly worthy of notice, some examples are: 2

The polyiodide group of organic ammonium compounds is particularly interesting, it being particularly rich in pentaiodides, while in inorganic chemistry there is only one pentiodide, *i.e.* casium pentaiodide. Hepa- and nona-iodides of organic ammonium bases are known, while inorganic analogues are not known. Examples of hepta- and nona-iodides are:³

$$\begin{split} \big[\mathrm{N}(\mathrm{CH_3})(\mathrm{C_2H_5})_3 \big] \mathrm{I}_7, \quad \big[\mathrm{N}(\mathrm{C_2H_5})_4 \big] \mathrm{I}_7, \quad \big[\mathrm{N}(\mathrm{C_6H_5})(\mathrm{CH_3})_3 \big] \mathrm{I}_7, \\ \big[\mathrm{N}(\mathrm{CH_3})_2(\mathrm{C_2H_5})(\mathrm{C_6H_5}) \big] \mathrm{I}_7, \\ \big[\mathrm{N}(\mathrm{CH_3})_4 \big] \mathrm{I}_9, \quad \big[\mathrm{N}(\mathrm{C_2H_5})(\mathrm{CH_3})_3 \big] \mathrm{I}_9. \end{split}$$

Beyond tri-, penta-, hepta- and nona-iodides, others are described in the literature, i.e. sexqui-, di-, tetra-, and hena-iodides. These compounds are either the addition products of simple iodides or the result of the combination of two periodides, or the result of several molecules of a halide adding on to a halogen, thus: $2RI + I_2$, etc.

Several constitutional formulæ for such polyhalides have been proposed. In particular, those which group the halogens around the positive atom have met with most favour. This supposition is, however, quite untenable, for the polyhalides have (externally) the character of addition compounds, and all their physical and

¹ Filhol, Berzelius Jahresber., 20 (2), 110 (1845); Wells and Wheeler, Amer. J. Sci., (3) 44, 42 (1892); Weinland and Schlegelmilch, Zeitsch. anorg. Chem., 30, 134 (1902).

² Hantzsch, Ber., 28, 2754 (1895).

³ Geuther, Annalen, 240, 72 (1887).

⁴ Jörgensen has described different periodides of alkaloides and metal ammonium compounds. (Om den saakaldte Herapathit og lignende Acidperjodider Vidensk. Selsk. Skr. 5 te Raekke, naturvidenskabelig og mathematisk Afd. 12 te Bd. I.)

chemical behaviour is contrary to the assumption that they are linked to the positive radicle. On this account it is nowadays widely accepted that in the polyhalides we have examples of molecular compounds, an opinion first expressed by Geuther, and thoroughly worked by him in connection with his work on polyiodides. Walls and Wheeler reject this explanation when it is applied to triiodides.

The characteristics of this class of compound are most distinct in compounds with the general formula: R(ICl₄), the first representatives of which (the potassium, ammonium, and magnesium salts) were described by Filhol.³ From these compounds iodine trichloride can be extracted with carbon tetrachloride,⁴ which proves that they are the addition-products of RCl and ICl₃. And since iodine trichloride has the formula:

it follows that these addition compounds are simply tetrachloriodates, and correspond in constitution to chloroauriates:

$$\begin{bmatrix} Cl \\ ClICl \\ Cl \end{bmatrix} R \quad and \quad \begin{bmatrix} Cl \\ ClAuCl \\ Cl \end{bmatrix} R$$

According to this conception cæsium pentabromide and cæsium pentaiodide will have constitutions corresponding to the tetrachloriodates, thus:

$$\begin{bmatrix} I \\ I \\ I \end{bmatrix} and \begin{bmatrix} Cl \\ ClICl \\ Cl \end{bmatrix}$$

Trihalogens are to be considered as addition compounds formed by the addition of metallic halides and halogenmonohalide, thus, compounds with the general formula RICl₂ become R(ClICl), and therefore are called dichloriodates.

With reference to the constitution of all possible combinations of the polyhalogen radicle X₃, it is to be assumed that in them the most positive halogen atom acts as the central atom, and the

¹ Annalen, 240, 82 (1887).

² Zeitsch. anorg. Chem., 1, 85 and 442 (1892).

³ Berzelius Jahresber., 20 (2), 110 (1845).

Weinland and Schlegelmilch, Zeitsch. anorg. Chem., 30, 136 (1902).

non-existence of trichlorides is to be attributed to chlorine being unable to act as a central atom.

While the complex acid radicle of polybromides contains as a maximum only five bromine atoms, complex acid radicles in the case of iodine containing seven and nine atoms are known. The constitution of such radicles is, perhaps, to be explained on the assumption that either one or both of the free co-ordination positions of the central iodine in

$$\begin{bmatrix} \mathbf{I} & \mathbf{i} \\ \mathbf{i} & \mathbf{i} \\ \mathbf{i} \end{bmatrix}$$

are occupied by iodine molecules.

(h) Mixed Types of Halogeno Salts.

Up to the present we have only considered compounds prepared from the same halogens. But it is possible for different halides to combine together to form halides of the higher order, thus bromides with chlorides, iodides with bromides, etc. Such halogeno salts are known as mixed salts. The following series of compounds illustrate the class:—

$$\begin{split} & \left[\text{Tl}_{\text{Cl}_{3}}^{\text{Br}_{3}} \right] \text{Tl}_{3}^{-1} \quad \left[\text{Tl}_{\text{Br}_{2}}^{\text{Cl}_{4}} \right] \text{Tl}_{3}^{-1} \quad \left[\text{Tl}_{\text{Cl}_{2}}^{\text{Br}_{4}} \right] \text{Tl}_{3}^{-1} \quad \left[\text{Tl}_{\text{Cl}_{3}}^{\text{Br}_{2}} \right] \text{Tl}_{2}^{-2} \\ & \left[\text{Cd}_{\text{Cl}_{2}}^{\text{Br}_{2}} \right] (\text{H. Papaverine})_{2}^{-3} \quad \left[\text{Hg}_{\text{Br}_{2}}^{\text{Cl}_{2}} \right] \text{K}_{2}^{-4} \quad \left[\text{Hg}_{\text{Br}_{2}}^{\text{Cl}_{2}} \right] \left[(\text{C}_{6} \text{H}_{4} \text{CH}_{3})_{2} \text{I} \right]^{5} \\ & \left[\text{Pt}_{\text{Cl}_{2}}^{\text{Br}_{4}} \right] (\text{HC}_{6} \text{H}_{13} \text{N})_{2}^{-6} \quad \left[\text{Pt}_{\text{Br}_{2}}^{\text{Cl}_{4}} \right] \text{R}_{2}^{-7} \quad \left[\text{Pt}_{\text{Br}_{2}}^{\text{Cl}_{4}} \right] \text{K}_{2}^{-8} \\ & \left[\text{Hg}_{\text{Cl}_{1}}^{\text{Br}_{2}} \right] \text{Cs}^{-9} \quad \left[\text{Hg}_{\text{Cl}_{2}}^{\text{Br}_{2}} \right] \text{Cs}_{3}^{-9} \quad \left[\text{Hg}_{2}^{\text{Br}_{4}} \right] \text{Cs}^{-9} \\ & \left[\text{Hg}_{5}^{\text{Cl}_{1}} \right] \text{Cs}^{-9} \quad \left[\text{Sn}_{\text{Cl}_{2}}^{\text{Br}_{2}} \right] (\text{NH}_{4})_{2} + \text{H}_{2} \text{O}^{-10} \end{split} \right. \end{split}$$

- ¹ Cushmann, Amer. Chem. J., 24, 222 (1902).
- ² Thomas, Compt. rend., 132, 80 (1901).
- ³ Jahoda, M., 7, 506 (1886).
- 4 Harth, Zeitsch. anorg. Chem., 14, 343 (1897).
- ⁵ MacCrae, Ber., 28, 98 (1895).
- 6 Markownikoff, J. Russ. Phys. Chem. Soc., 30, 151 (1898).
- ⁷ Hermann, Ber., 22, 3076 (1889).
- ⁸ Miolati, Zeitsch. anorg. Chem., 14, 237 (1897).
- ⁹ Wells, ibid., 2, 416 (1892).
- 10 Raymann and Preis, Jahrg., 1884, p. 436.

$$\begin{bmatrix} Pb_{Br_{2}}^{Cl_{2}} (NH_{4})_{2} + 4H_{2}O^{1} & Pb_{2Br}^{Cl_{4}} NH_{4}^{1} & Pb_{Cl}^{Br_{4}} NH_{4}^{1} \\ Au_{Br}^{Cl_{3}} H. & Hyoscine^{2} & Au_{Br}^{Cl_{3}} H. & Hyoscyanamine^{2} \\ Au_{Br}^{Cl_{3}} H. & Atropine^{2} & Au_{Cl}^{Br_{3}} H. & Aminocyklohexane^{3} \\ Sb_{Br}^{Cl_{3}} H. & Atropine^{2} & Au_{Cl}^{Br_{3}} H. & Aminocyklohexane^{3} \\ Sb_{Br}^{Cl_{3}} K + H_{2}O^{4} & Sb_{Br_{3}}^{Cl_{3}} K_{3}^{4} & Zn_{Cl_{2}}^{L_{2}} (H. & Papaverine)_{2}^{5} \\ Cd_{Cl_{2}}^{I_{2}} (H. & Papaverine_{2})^{5} & Hg_{Cl_{2}}^{I_{2}} Cs_{2}^{6} & Hg_{Cl_{2}}^{I_{2}} Ag_{2}^{7} \\ Hg_{Cl_{2}}^{I_{2}} [S_{CH_{3}}^{(C_{2}H_{5})_{2}}]^{8} & Hg_{Cl_{2}}^{I_{2}} [S_{CH_{3}}^{(C_{2}H_{5})_{2}}]^{9} & Hg_{Br}^{I_{2}} Cs^{10} \\ Hg_{Br_{2}}^{I_{2}} Cs_{2}^{11} & Hg_{Br_{3}}^{I_{2}} Cs_{3}^{12} & Pb_{Cl_{3}}^{I_{2}} NH_{4} + 2H_{2}O^{13} \\ Pb_{Cl_{3}}^{I_{2}} (NH_{4})_{3}^{14} & Pb_{Cl_{4}}^{I_{2}} (NH_{4})_{4} + 2H_{2}O^{15} \\ Pb_{Br}^{I_{2}} NH_{4} + 2H_{2}O^{13} & Pb_{2Br}^{I_{4}} NH_{4}^{13} \\ [Bi_{2I_{3}}^{Cl_{6}}] [P(C_{2}H_{5})_{4}]_{3}^{16} & Bi_{2I_{3}}^{Cl_{6}} [Sb(C_{2}H_{5})_{4}]_{3}^{17} \\ [Bi_{Br_{3}}^{Br_{3}} (NH_{4})_{2} + 2\frac{1}{2}H_{2}O^{18} & Bi_{2I_{3}}^{Br_{6}} [Sb(C_{2}H_{5})_{4}]_{3}^{10} \end{bmatrix}$$

- ¹ Fonzes-Diacon, Bull. Soc. Chim., (3) 17, 346 (1897).
- ² Jowett, Trans., 71, 679 (1897).
- ³ Markownikoff, J. Russ. Phys. Chem. Soc., 30, 151 (1898).
- ⁴ Atkinson, Chem. News, 47, 175 (1883).
- ⁵ Jahoda, M., 7, 515 (1886).
- 6 Wells, Zeitsch. anorg. Chem., 2, 418; Penfield, ibid., 1892, p. 423.
- ⁷ Lea, Sill. J., (3) 7, 34; Orme, Chem. News, 30, 205 (1874).
- ⁸ Patein, Bull. Soc. Chim., (3) 2, 164; Smiles, Proc. Chem. Soc., 15, 240.
- Patein, loc. cit.
- 10 Wells, Zeitsch. anorg. Chem., 2, 418; Penfield, ibid., 1892, p. 425.
- Wells, loc. cit.; Penfield, ibid., p. 423.
- 12 Wells, ibid.; Penfield, ibid., p. 420.
- 13 Fonzes-Diacon, Bull. Soc. Chim., 17, 346 (1897).
- ¹⁴ Völkel, Behrens, Pogg. Ann., 62, 152 (1844).
- 15 Poggiale, Compt. rend., 20, 1180 (1845).
- 16 Jörgensen, J. pr. Chem., (2) 3, 345 (1871).
- 17 Beilstein, Edition III., 1, 1515.
- 18 Linau, Pogg. Ann., 111, 240; Wurtz, Dict., 1, 608.
- 19 Jörgensen, J. pr. Chem., (2) 3, 343 (1871).

It is interesting to note that halides and polyhalides can combine together to form complex salts. To this class belong the following peculiar compounds described by Wells.¹

¹ Zeitsch. anorg. Chem., 4, 346 (1893).

$2PbI_{2} \cdot 3KI \cdot I + 4H_{2}O, \ 2PbBr_{2} \cdot 3KBr \cdot Br. + 4H_{2}O, \ and \ K_{3}[Pb_{2}(BrI)_{8}] + 4H_{2}O$

(i) On the Halogeno Acids.

(a) The Halogeno Acids of the Metals.

The halogeno acids from which the halogeno salts are derived have been little examined up to the present, and it is very desirable that this class of compounds should be thoroughly worked out. But it must be pointed out that these compounds are very difficult to deal with, because most of them are very unstable, and it is consequently difficult to prepare them in the pure state. Engle's exact and painstaking work on the chloro acids is the best that has as yet been done; and yet there are many gaps even amongst these acids which ought to be filled. The following is a list of all the halogeno acids that the author could find in the literature:—

(a) CHLORO ACIDS.

 $\begin{array}{l} (ZnCl_2)_2HCl + 2H_2O,^1 \ ZnCl_2 \ . \ HCl + 2H_2O,^2 \ CuCl_2 \ . \ HCl + 3H_2O,^3 \\ CuCl_2 \ . \ 2HCl + 5H_2O,^4 \ CdCl_2 \ . \ 2HCl + 7H_2O,^5 \ SnCl_2 \ . \ HCl \\ + 3H_2O,^6 \ HgCl_2 \ . \ 2HCl + 7H_2O,^7 \ (HgCl_2)_3HCl + 14H_2O,^7 \\ (HgCl_2)_3HCl + 6H_2O,^7 \ (HgCl_2)_2HCl + 4H_2O^7, \ (HgCl_2)_3HCl \\ + 5H_2O,^7 \ (HgCl_2)_3HCl + XH_2O,^7 \ (SbCl_3)_2HCl + 2H_2O,^8 \\ (BiCl_3)_2HCl + 3H_2O,^9 \ FeCl_3 \ . \ HCl + 2H_2O,^{10} \ AuCl_3 \ . \ HCl \\ + 4H_2O,^{11} \ TlCl_3 \ . \ HCl,^{12} \ PtCl_4 \ . \ 2HCl + 6H_2O,^{13} \ SnCl_4 \ . \\ 2HCl + 6H_2O,^{14} \ SbCl_5 \ . \ 5HCl + 11H_2O.^{15} \end{array}$

- ¹ Engel, Compt. rend., 102, 1069 (1886).
- ² Engel, *ibid.*, 1886, p. 1070.

³ Engel, *ibid.*, **106**, 273 (1888).

- ⁴ Sabatier, ibid., 1888, p. 1724; Engel, ibid., 107, 178 (1888).
- ⁵ Berthelot, ibid., 91, 1024 (1880).
- ⁶ Engel, ibid., 106, 1399 (1888).
- ⁷ Ditte, Ann. Chim. anal., (5) 22, 551 (1881).
- 8 Engel, Compt. rend., 106, 1798 (1888).
- ⁹ Engel, *ibid.*, 1888, p. 1799.
- ¹⁰ Engel, *ibid.*, **104**, 1709 (1887).
- ¹¹ Thomsen, Ber., 10, 1633 (1877).
- 12 Thomas, Compt. rend., 134, 545 (1902).
- 13 Weber, Pogg. Ann., 131, 441 (1867).
- 14 Engel, Compt. rend., 103, 213 (1886).
- 15 Engel, ibid., 106, 1799 (1888).

(b) Bromo Acids.

CuBr₂. HBr + $2H_2O_1^1$ 3CuBr₂. $2HBr + 6H_2O_1^1$ HgBr₂. HBr + $4H_2O_2^2$ IrBr₃. $3HBr + 3H_2O_3^3$ AuBr₃. HBr + $5H_2O_3^4$ PtBr₄. $2HBr + 9H_2O_3^5$ SnBr₄. $2HBr + 8H_2O_3^6$ TeBr₄. HBr + $5H_2O_3^6$ TeBr₄. HBr

(c) IODO ACIDS.

AgI + HI, $HgI_2 . HI$, $SnI_2 . HI$, $PbI_2 . HI + 5H_2O$, $BiI_3 . HI . 4H_2O$, $PtI_4 . 2HI + 9H_2O$, $TeI_4 . HI + 8H_2O$.

(d) MIXED TYPES OF HALOGENO ACIDS.

TlCl₂Br . HCl,¹⁵ TlClBr₂ . HCl,¹⁵ TlCl₂Br . HBr,¹⁵ TlClBr₂ . HBr.¹⁵

- ¹ Sabatier, ibid., 118, 1260.
- ² J. pr. Chem., (2) 11, 283 (1875).
- ² Birnbaum, Bromverbindungen des Iridiums, Dissertation, Göttingen, 1864.
 - ⁴ Thomsen, J. pr. Chem., (2) 13, 337 (1876).
 - ⁵ Halberstadt, Ber., 17, 2962 (1884).
 - ⁶ Seubert, ibid., 20, 794 (1887).
 - ⁷ Thomas, Compt. rend., 134, 545 (1902).
 - ⁸ Berthelot, ibid., 91, 1024 (1880).
 - ⁹ Neumenn, Wien. Monatsh., 10, 240 (1890).
 - 10 Young, J. Amer. Chem. Soc., 19, 851 (1897).
 - 11 Berthelot, Compt. rend., 91, 1024 (1880).
 - 12 Arppe, Pogg. Ann., 64, 237 (1845).
 - 13 Topsoë, N. Arch. phys. nat., 38, 207; Chem. Centr., 1870, p. 683.
 - 14 Metzner, Compt. rend., 124, 1448 (1897).
 - 15 Thomas, ibid., 134, 545 (1902).

The examination of this list of halogeno acids shows that almost all those acids which have been separated in the pure state contain water, and this is true even when the mother halide crystallizes from aqueous solution without any water of crystallization. Thus, SbCl₃ does not combine with water, and yet the chloro acid has the composition

$Cl_3Sb \cdot ClH + 2H_2O$

In like manner bismuth chloride crystallizes anhydrous from aqueous solution, but the chloro acid corresponds to the formula

$$(BiCl_3)_2ClH + 3H_2O$$

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Engel noticed these peculiarities, and he also pointed out that the addition of one molecule of hydrochloric acid always resulted in the addition of at least two molecules of water, so that in the cases where two halogeno acids were derived from the same halogeno acid anhydride:

$$(ZnCl_2)_2ClH + 2H_2O$$
 and $ZnCl_2 \cdot 2ClH + 4H_2O$ $CuCl_2 \cdot ClH + 3H_2O$ $CuCl_2 \cdot 2ClH + 5H_2O$

at least two molecules of water were taken up for every one of hydrochloric acid. Hence, the formation of these chloro acids is not brought about by the addition of hydrochloric acid, but by the addition of the hydrate $ClH + 2H_2O$, which Pierre and Puchot were the first to isolate in the free state. Since this hydrate has in

all probability the constitution $ClH = OH_2$, it follows that the halo-

geno acids are to be considered as oxonium compounds formed by the addition of a halogeno acid to water. The consideration of quite another class of phenomena leads to the same conclusion. The dihydrate of cupric chloride ($CuCl_2 + 2H_2O$) is blue, but the chloro acids of copper containing three and five molecules of water have colours between granate red and hyacinth red, and this agrees with the colour of the monohydrate, $CuCl_2 + H_2O$. It is, therefore, certain that in the chloro acids of copper, not more than one molecule of water is bound to the copper, so that their constitutions are expressed by the formulæ:

$$\left[Cu_{Cl_3}^{OH_2} \right] H \cdot (OH_2)_2 \quad and \quad \left[Cu_{Cl_4}^{OH_2} \right] [H(OH_2)_2]_2$$

(β) The Halogeno Acids of Hydrogen.

The halogeno acids of the metals belong to the acid halide salts, and the question naturally arises as to what relation certain acid halide salts, in which the acid character is not strongly evident, e.g. a series of acid fluorides, are to those of the metals. Such acid fluorides are:

FK. HF,
$$Co(NH_3)_6F_3$$
. 3HF, etc.

The existence of these and similar compounds is doubtless related to the fact that hydrofluoric acid is not mono- but bimolar. In order to explain this bimolar condition of hydrofluoric acid, the constitutional formula HF = FH is much used, and it derives a certain amount of support from the analogous formation of double

fluorides. However, there can be no doubt that this formula is incorrect, for it is highly improbable that the two fluorine atoms are united together. This is to be seen in analogy which exists between the fluoro salts and the other halogeno salts, and in hydrofluoric acid the hydrogen must play the chief part in the polymerization of the molecule, for when alkyl is substituted for hydrogen the capacity for polymerization ceases, for the alkyl fluorides are monomolecular. This polymerization, therefore, can only be possible when hydrogen becomes the central atom of the halogen acidic anhydride. This being so it follows that the bimolecular hydrofluoric acid has the following constitutional formula: H(F,H,F), and the acid fluorides are to be looked upon as salts of hydrodifluoric acid.

Both the properties of hydrofluoric acid, i.e. the trifling electrolytic dissociation, its weakness as an acid, etc., as well as the existence of acid fluorides, find a simple and satisfactory explanation in the formula.

In passing it may be noted that the hydrochloric acid has also a slight capacity for polymerization, for it is bimolar in formic acid.1

(k) Double Cyanides, Double Thiocyanides, etc.

Hydrocyanic acid behaves in many cases, as is well known, as if it were a halogen acid, with the result that cyanides are comparable to bromides, chlorides, etc. It is accordingly found that prussic acid and the cyanides form complex compounds which are comparable to those of the halogen acids and their salts. The combination of cyanides produces cyano salts which are remarkable for their great stability. Their composition and stoichiometrical behaviour are strikingly analogous to the halogeno salts. There is, therefore, no doubt that the formation of a cyano salt takes place in the same way as the halogeno salts. In order to give some idea of this class of compounds a few are appended, but the list is by no means exhausted:—

¹ Zanninovich-Tessarin, Zeitsch. physikal Chem., 19, 251 (1896).

This list shows that with the single exception of [MoCy₈]K₄, the maximum number of cyanide radicles linked to the central atom is six—the same number which was found to be the maximum in the case of oxygen and halogeno salts.

The double thiocyanide are so exactly similar to the cyano and halogeno salts that they need not be discussed. A valuable list of these compounds has been prepared by Grossman.¹

(1) Mixed Salts prepared from Halides, Cyanides, and Thiocyanides.

Just as different halides combine to form mixed halogeno salts, so in like manner is it possible for halides to combine with cyanides or thiocyanides, or cyanides with thiocyanides to form complex salts, the acid radicle of which contains different components. Such salts are therefore called mixed salts. Compounds of this class are exemplified by the following:

$$\begin{split} & \left[Hg_{Cl}^{Cy_2} \right] R^{\, 1} \quad \left[Hg_{Br}^{Cy_2} \right] R^{\, 1} \quad \left[Hg_{I}^{Cy_2} \right] R^{\, 1} \quad \left[Hg_{SCN}^{Cy_2} \right] R^{\, 2} \\ & \left[Hg_{Cl}^{(SCN)_2} \right] R^{\, 3} \quad \left[Hg_{Br_2}^{(SCN)_2} \right] R_{2}^{\, 3} \quad \left[Hg_{I_2}^{(SCN)_2} \right] R_{2}^{\, 4} \quad \left[Hg_{Br_2}^{SCN} \right] R^{\, 3} \\ & \left[Cd_{Cl_2}^{(SCN)_2} \right] R_{2}^{\, 4} \quad \left[Cd_{Br}^{(SCN)_2} \right] R^{\, 4} \\ & \left[Cu_{Cy_3}^{(SCN)} \right] R_{3}^{\, 4} \quad \left[Cu_{2Cy_3}^{(SCN)_2} \right] R_{3}^{\, 4} \\ & \left[Pt_{Cl_2}^{Cy_4} \right] R_{2}^{\, 5} \quad \left[Pt_{Br_2}^{Cy_4} \right] R_{2}^{\, 5} \quad \left[Au_{Br_2}^{Cy_2} \right] R^{\, 6} \quad \left[Au_{I_2}^{Cy_2} \right] R^{\, 7} \end{split}$$

- ¹ Mathewson and Wells, Amer. Chem. J., 30, 432 (1903).
- ² Grossman, Ber., 37, 1258 (1905).
- ³ Grossman, ibid., 85, 2665, 2945 (1903).
- 4 Grossman, Zeitsch. anorg. Chem., 37, 407 (1903).
- ⁵ Holst, Bull. Soc. Chim., (2) 22, 347 (1874).
- 6 Lindbom, ibid., (2) 29, 416 (1878).
- ⁷ Blomstrand, J. pr. Chem., (2) 3, 213 (1871).

2. Compounds of Higher Order with Oxides, Sulphides, etc.

- 1. The Addition Compounds.
- (a) General Considerations.

Those oxygen compounds which are formed by the combination of two or more oxides are called oxygen compounds of higher

¹ Zeitsch. anorg. Chem., 37, 411 (1903).

order. A certain class of these compounds, the oxygen salts, have had dualistic formulæ given them, thus:

These formulæ had to give way to unitarian formulæ, because the idea of the individual existence of the component oxides in such compounds advocated by the formulæ was shown to be untenable. We have no desire to revive the dualistic formulæ in its original form, nevertheless dualistic formulæ will be often used in what follows, because they offer a point of view from which the systematics of inorganic compounds (i.e. the production of compounds of higher order through the combination of those of the first order) can be clearly examined. Moreover, this method of treatment has the additional advantage of bringing out the relations between the double oxides and other classes of compounds. Finally, dualistic formulæ correctly represent the constitution of the double oxides as molecular compounds.

On reasons deduced from the theory of valency, as we have already pointed out, the dualistic conception of the double oxides underwent a peculiar change, which it was believed explained the cause of the combination of oxides and the manner in which this took place. But we have seen further that this explanation is incorrect, for the capacity of combining together to form compounds of higher order does not only belong to oxides but to all compounds of the first order. The cause of this behaviour has been shown to be due to the residual affinity of the elementary atoms in the binary compounds and to be brought about through the action of auxiliary valencies. In the special case of the formation of oxygen salts, the union is brought about by the activity of the auxiliary valencies on the central atom of the acidic oxide and those on the oxygen atom of basic oxide:

Oxygen acids and salts are therefore primarily molecular compounds; they differ from other molecular compounds in that they pass into ordinary valency compounds owing to the divalency of oxygen and the great mobility of the hydrogen or metallic atoms.

(b) Quantitative Ratios in the Formation of Oxygen Acids and Salts.

Having made clear the general lines upon which oxygen acids and salts are formed, let us turn our attention to the discussion of the rules governing the quantitative formation of these reactions.

Firstly, an oxygen acid anhydride can combine with varying quantities of other oxides; for example, such an anhydride can combine with several molecules of water, thus producing acids, and the compound richest in water is called the ortho-form. Such ortho-forms are—

$$CO_2 + 2H_2O$$
, $SiO_2 + 2H_2O$, $P_2O_5 + 3H_2O$, etc.

The ortho-forms, as such, are often unstable, although their salts or esters can be prepared, and for their theoretical treatment the existence of hypothetical hydrates are often assumed, although it has not been possible to prepare either salts or esters to justify such assumptions: e.g. the hydrate of nitric acid, $N_2O_5 + 5H_2O = 2N(OH)_5$.

The practice of making such unfounded suppositions must be vigorously opposed, for they are only too suited for misrepresenting the actual behaviour of the compounds in question. The existence of the hydrate N(OH)₅ appears to be quite impossible, because the co-ordination number of nitrogen is never greater than four.

Those acids poorer in water are called the <u>meta-forms</u>, thus— $CO_2 + H_2O$, $SiO_2 + H_2O$, $P_2O_5 + H_2O$.

In working out the law governing the quantitative formation of oxygen acids and salts it is of importance to learn the maximum number of oxide molecules which a second oxide can take up. With this object let us compare with one another the composition of those acids and salts which are richest in oxygen, using the following acids for this comparison:

 $HClO_4$, $HMnO_4$, $HRuO_4$; H_2SO_4 , H_2SeO_4 , H_2MnO_4 , H_2CrO_4 , H_2MoO_4 ; H_2WO_4 , H_2RuO_4 , H_2OsO_4 , H_2FeO_4 ; H_3PO_4 , H_3AsO_4 , H_3VO_4 , H_3NbO_4 , H_3TaO_4 ; H_4SiO_4

This comparison clearly shows that four is the maximum number of oxygen atoms which are linked to any central metallic atom. This limiting number agrees with the number of oxygen atoms in the highest oxides RuO4 and OsO4, and these oxides no longer have the capacity for the formation of double oxides. In a few cases acid radicles containing still more oxygen are to be observed. Periodic acid was earlier the only example of this description, it contains the complex radicle IO6; as the composition of the following periodates make clear:

$$H_5(IO_6)$$
, $Ba_5(IO_6)_2$, $Li_5(IO_6)$, $Fe_5(IO_6)_2$, $Ag_5(IO_6)$, $Hg_5(IO_6)$, $Hg_5(IO_6)_2$ and $Cu_5(IO_6)_2 + 5H_2O$

The work of Burton and Hutchins (jun.) 1 had made it certain that in telluric acid we have another acid complex very rich in oxygen, i.e. TeO6. The following series of salts have been R_{0} R_{0} N_{0} N_{0 prepared:

$$Ag_6[TeO_6]$$
, $Hg_3[TeO_6]$, $Zn_3[TeO_6]$ and $Cu_3[TeO_6]$

The so-called normal tellurates—

$$Ag_2TeO_4 + 2H_2O$$
, $Rb_2TeO_4 + 2H_2O$, $Cs_2TeO_4 + 2H_2O$, $Na_2TeO_4 + 2H_2O$, $K_2TeO_4 + 2H_2O$, $HgTeO_4 + 2H_2O$,

must therefore be considered as the acid salts of orthotelluric acid, (TeQ6) H. It is interesting to note that both elements which form acids with the adicle MO, occupy contiguous positions in the periodic system

Since the pormal tellurates are isomorphous with the osmiates, 2 e.g.

it is very probable that osmiates are the acid salts of orthoosmic acid, $(O_6O_6)H_6$. Potassium ruthenate has the formula $K_2RuO_4 + H_2O_5$ and therefore is probably the acid salt of an acid H,RuO5. Chromic acid has also the capacity of forming salts of the type R₄(MO₅); two salts of this description have been prepared:

$$Na_4(CrO_5) + 13H_2O^3$$
 and $Ca_2CrO_5 + 3H_2O^4$

We therefore have two limiting types of oxygen acids, the one containing four oxygen atoms in the acid radicle, and the other Both limiting radicles, MO4 and MO6, correspond with the

J. Amer. Chem. Soc., 27, 1157 (1905).

² Retgers, Zeitsch. anorg. Chem., 12, 98 (1896).

Mylius and Funk, Wissenschaft. Abh. der Phys.-Tech. Reichsanstalt, 3, 449 (1900); Schreinemakers, Zeitsch. physikal. Chem., 55, 91 (1906).

^{&#}x27; Mylius and Wrochen, Ber., 33, 3689 (1900).

principal types of the complex radicles of other groups of compounds of the higher order; the one corresponds to the plane and the other to the spacial co-ordination number of the atoms.

(c) On Polymeric Oxides.

Our discussion up to the present has been limited to those double oxides which are formed by union of two different oxides. But the question arises, as to whether it is not possible for oxides of the same kind to combine together. We usually assume that the simple oxides are monomolar, but this is very seldom true. As a general rule the oxides are polymerized, and this polymerization has to be referred to the same causes as the combination between two dissimilar oxides. The formation of complexes from heterogeneous oxides consequently will correspond to the formation of complexes from similar oxides, and we can term the latter process "auto-complex formation." That many oxides are polymers may be deduced from different phenomena, thus, many oxides such as metallic oxides, etc., have a very high melting-point. Even in cases where the melting-point is relatively low, as in the case of arsenic trioxide, determinations of the molecular weight have shown that polymeric forms, e.g. $(As_2O_3)_2$, are stable. Another example of this type is water, which, as is well known, is polymeric.

The polymerization of oxides can be structurally explained in the same way that was used to explain the union between dissimilar oxides. If we imagine, for example, SO₃ to have free auxiliary valencies on sulphur and oxygen, then it would be possible for these to be saturated according to the scheme—

Whether this polymeric oxide is an auxiliary valency compound, or, since a displacement of the valencies is possible, an ordinary valency compound, as the following:

is a futile question, and one which is of only secondary importance for the constitutional behaviour of such polymeric oxides. It should, however, be noted that the auxiliary valency formulation must not be excluded, because quite similar phenomena have been noted amongst the halides, and in these cases a transportation in the ordinary valency formulæ is impossible, e.g.:

$$\begin{array}{cccc} Cl & Cl & \\ Cl-Al & Cl-Al & \rightarrow & Cl & Cl \\ Cl-Al & Cl-Al & \rightarrow & ClAl & ClAl \\ Cl & Cl & Cl & Cl & Cl \\ \end{array}$$

(d) Polynuclear Oxygen Acids and Salts.

Some polymeric oxides are so stable that they can act as acid anhydrides in the formation of compounds of the higher order. Bimolar chromium trioxide is an example of this class:

Amongst the chromic acids tri- and tetra-chromates, (CrO₃)3OR₂ and (CrO₃)4OR₂, are even known. Our method of formulation offers a simple and satisfactory explanation of the formation of such compounds from neutral salts and simple acid anhydrides:

This polymerization is not confined to oxides of the first order but also may be observed in double oxides. The formation of acid salts from monobasic acids may possibly be a change of this description, e.g. the iodine acids:

¹ Jäger and Krüss, Ber., 22, 2034 (1889).

This capacity of the oxides for polymerization is particularly noticeable in some elements, e.g. silicon, molybdenum, tungsten, vanadium, niobium, and tantalum.

The difficulties which have to be overcome in the establishment of the constitution of polymeric oxides, *i.e.* the manner in which the addition of the acid anhydride to the neutral salt takes place, render an exhaustive theoretical treatment of polynuclear oxygen acids impossible for the present. Nevertheless we may point out some interesting facts.

There exists a series of complex salts which are formed by the addition of the trioxides of molybdenum and tungsten to different acids, and the resulting salts contain as a maximum either six or two molecules of MoO₃ or WO₃. This is true of the following series:

The constitution of these compounds may be explained by assuming that the parent acids have taken up six molecules of MoO_3 or WO_3 or six double molecules $(MoO_3)_2$ or $(WO_3)_2$, and the addition compounds are constituted therefore similarly to the hydrates containing 6 and 12 molecules of water, these hydrates will be discussed later. Kieseltunstic acid has therefore the following constitution:

The constitution of polymolybdates and of polytungstates can also be considered from this point of view.

Ordinary ammonium molybdate has the formula

$$(NH_4)_6Mo_7O_{24} + 24H_2O$$

the corresponding potassium and sodium salts are also known. They may therefore be considered as orthomolybdates, MoO_6R_6 , in which each of the six oxygen atoms have taken up one molecule MoO_3 :

$$(MoO_6)R_6 + 6MoO_3$$

The paratungstates have had the formula

$$R_6W_7O_{24}$$

¹ Kehrmann, Zeitsch. anorg. Chem., 7, 406 (1894).

assigned to them, and these also may be given the structural formula:

$$(WO_6)R_6 + 6WO_3$$

Other workers have formulated the paratungstates as $K_{10}W_{12}O_{41}$, according to which they could be considered as double salts of $R_4W_5O_{17}$ and $R_6W_7O_{24}$. As a matter of fact, when preparing sodium paratungstate the salt $Na_4W_5O_{17}+11H_2O$ is often found to be present; and Marignac has shown that on recrystallizing the paratungstate in the presence of a little soda, the salt $Na_6W_7O_{24}+16H_2O$ crystallizes out.

The formation of all these compounds is consequently due to the addition of either salts or acids to the acid anhydride. Two simple examples will illustrate this behaviour. When potassium sulphate takes up a molecule of chromium trioxide, forming potassium chromato-sulphate, the change can be expressed by the following equation:

$$O \begin{pmatrix} O & O \\ O C r + O S & O \end{pmatrix} K_2 = O \begin{pmatrix} O & O \\ O C r & O S & O \end{pmatrix} K_2$$

and the union of iodates with chromium trioxide is to be expressed in like manner, thus:

$$O \begin{pmatrix} O & O \\ O & + O \\ O \end{pmatrix} K = O \begin{pmatrix} O & O \\ O & O \\ O & O \end{pmatrix} K$$

However, it will only become possible, after extended researches, to decide definitely how the different components unite together in each particular case.

(e) On Peroxides.

Simple peroxides, Me₂O₂, can be considered as being formed by the union of a divalent oxygen atom with the elementary atom in question. For the constitution of such compounds two possibilities present themselves, *i.e.*

The former is strictly in accordance with the doctrine of valency, and belongs to a great many organic derivatives of hydrogen peroxide. The latter is only partly a valency formula, i.e. the linking

of the two metallic atoms, but the linkings of the two oxygen atoms are not in accordance with the doctrine of valency. Of course it is simplest to bind the second oxygen to the first by two valencies, thus making the latter tetravalent. Yet it must be remembered that this conception presupposes the equivalence of these new valencies for hydrogen and oxygen—an idea which may be developed on paper but is not borne out by experiment. A more accurate idea of the constitution of a peroxide is obtained on comparing water and the simple metallic oxides with the hydrogen and metallic compounds of other metalloids and the peroxides with the products obtained by the addition of oxygen to these compounds.

		Binary compounds.	Monoxides.	Dioxides.	Trioxides.	Tetroxides.
Chlorides . Sulphides . Phosphides		$ m RC1 \\ m R_2S \\ m R_3P$	RCIO R ₂ SO R ₃ PO	$ RCIO_2 $ $ R_2SO_2 $ $ R_3PO_2 $	$RClO_3$ R_2SO_3 R_3PO_3	HClO ₄ R ₂ SO ₄ R ₃ PO ₄
Oxides		R_2^{31}	$R_2^{32}OO$	$R_2^3OO_2$	R_2OO_3	34

The ordinary peroxides belong to the monoxides, the ozonides, first discovered in organic chemistry, belong to the dioxides, and the alkalisuperoxides, called by Baeyer ozone acid salts, to the trioxides. The latter oxides, of which we have two examples, K_2O_4 and Rb_2O_4 , are produced by the direct oxidation of the alkali metals, or by the action of ozone on the simple oxides:

$$K_2 + 2O_2 = K_2O_4$$
, $K_2O + O_3 = K_2O \cdot O_3$

According to this conception the ordinary peroxides as well as those richer in oxygen are to be considered as compounds of the higher order. As far as the monoperoxide, MeO₂, is concerned, it has been demonstrated that the group O₂ only occupies one coordination position. Thus, for example, on the chromium atom in chromium tetraoxide, three co-ordination positions remain free, as is shown by the existence of the ammonium and potassium cyanide compounds:

$$\operatorname{Cr} \left(\begin{array}{c} \operatorname{O}_4 \\ (\operatorname{NH}_3)_3 \end{array} \right)$$
 and $\operatorname{Cr} \left(\begin{array}{c} \operatorname{O}_4 \\ (\operatorname{Cy} K)_3 \end{array} \right)$

Chromium tetraoxide has therefore the constitutional formula

$${
m O_2} \ {
m OCr}$$

in which O₂ only occupies one co-ordination position. The isomorphism between oxyfluoro- and peroxofluoro-salts leads to the same results.

The fact that superoxides combine together to form complex oxides in a manner analogous to simple oxides offers nothing new in principle, but a few examples of such combinations may be given. Thus chromium tetraoxide combines with metallic peroxides:

$$O_{2}^{O_{2}} + O_{2}^{O_{2}} + O_{2}^{O_{2}} = O_{2}^{O_{2}} \cdot O_{2}^{O_{2}}$$
 $O_{2}^{O_{2}} + O_{2}^{O_{2}} + O_{2}^{O_{2}} = O_{2}^{O_{2}} \cdot O_{2}^{O_{2}} \cdot O_{2}^{O_{2}}$
 $O_{2}^{O_{2}} + O_{2}^{O_{2}} + O_{2}^{O_{2}} = O_{2}^{O_{2}} \cdot O_{2}^{O_{2}} \cdot O_{2}^{O_{2}}$

thus giving rise to a blue perchromate. The red perchromates are O prepared from a chromium diperoxide, ${\rm CrO_2} \atop {\rm O_2}$

$$2\text{CrO}_5 + 3(\text{NH}_4)_2\text{O}_2 = (\text{CrO}_5)_2[\text{O}_2(\text{NH}_4)_2]_3$$

The number of compounds produced by the combination of different peroxides is already very large. The following list well illustrates their variety:

$$\begin{split} \text{Na}_2\text{O}_2. \ \text{UO}_4, \ \ \text{Li}_2\text{O}_2. \ \text{UO}_4, \ \ (\text{BaO}_2)_2. \ \text{UO}_4, \ \ \text{BaO}_2. \ \text{UO}_4, \ \ \text{Na}_2\text{O}_2. \ \text{WO}_4 \\ + \ \text{H}_2\text{O}_2, \ \ \text{K}_2\text{O}_2. \ \text{WO}_4. \ \text{H}_2\text{O}, \ \ \text{K}_2\text{O}_2. \ \text{MoO}_4. \ \text{H}_2\text{O}_2, \ \ \text{K}_2\text{O}_4. \ \text{TiO}_3 + 10 \text{H}_2\text{O}, \\ \text{Na}\text{O}_2. \ \text{TiO}_3 + \frac{1}{2}\text{H}_2\text{O}, \ \ \text{BaO}_2. \ \text{TiO}_3, \ \ \text{Na}_2\text{O}. \ \text{C}_2\text{O}_5, \ \ \text{Na}_2\text{O}_2. \ \text{CO}_2 + 1\frac{1}{2}\text{H}_2\text{O}, \\ \text{Na}\text{O}_2. \ \ \text{CO}_2 + 3 \text{H}_2\text{O}, \ \ \text{BaO}. \ \ \text{V}_2\text{O}_7 \end{split}$$

(f) On Sulpho and Seleno Salts.

The formation of double sulphides from simple sulphides, and double selenides from simple selenides, corresponds quite naturally to the formation of double oxides. The existence of double tellurides has not as yet been observed.

The sulpho and seleno salts (i.e. those double sulphides and double selenides with salt-like properties) are the best known members of this group of compounds. The most stable sulpho salts are those formed with phosphorus, arsenic, and antimony, and their neighbouring elements in the carbon group, i.e. germanium and tin.

A few elements of the iron and platinum groups, as well as chromium, molybdenum, and tungsten, also display a capacity for the formation of sulpho salts.

The following list will serve to illustrate this class of compounds:—

$$\begin{split} &[PS_4]K_3,^1[PS_4]Na_3 + 8H_2O, [AsS_3]R_3, [As_2S_4]R_2, [AsS_4]R_3, [SbS_4]R_3, \\ &[GeS_6]Ag_8, [SnS_3]R_2, [SnS_4]R_4, [SnS_6]_{Pt_3}^{K_2}, [SnS_6]Pt_4, [SnS_6]_{Pt_3}^{Na_2}, \\ &[TlS_2]K, \end{split}$$

 $[HgS_2]K_2 + 5H_2O$,

[AuS]Na + 4H₂O, [PdS₃]Na₂, [Pd₃S₄]K₂, [Pd₃S₄]Ag₂, [PtS₆]^{K₂}_{Pt₃}, [PtS₆]^{Na₄}_{Pt₂}, [PtS₆]^{Na₂}_{Pt₃}, [PtS₆]Pt₄, [PtS₂]K₂,

 $[FeS_4]_{Cu_3}^{Na_2}, \ [FeS_4]_{Cu_3}^{K_2}, \ [Fe_2S_4]K_2, \ [Cr_2S_4]Na_2,$

[MoS₄]K₂, [MoS₄]Na₂, [WS₄]K₂, [WS₄]Na₂, etc.

The sulpho salts, as is well known, play an important part in mineral chemistry.

Seleno salts are only little known:

$$\begin{split} [SnSe_6]_{K_2}^{Pt_3,^3} \quad Na_3AsSe_3 + 9H_2O,^4 \quad KAsSe_3 + 2H_2O,^4 \quad K_2HPSe_3 \\ \quad + 2\frac{1}{2}H_2O,^5 \quad Na_3SbSe_4 + 9H_2O.^6 \end{split}$$

- Glatzel, Zeitsch. anorg. Chem., 4, 190 (1893).
- ² Schneider, Pogg. Ann., 148, 625 (1873).
- ³ Schneider, J. pr. Chem., (2) 44, 507 (1891).
- 4 Clever and Muthmann, Zeitsch. anorg. Chem., 10, 115 (1895).
- ⁵ Clever and Muthmann, ibid., 13, 191 (1897).
- 6 Hofacker, Annalen, 107, 6 (1858).

A glance at this list will show that in many cases the number of sulphur atoms in the sulpho salts is identical with the number of oxygen atoms in the corresponding salts of the same element.

The maximum co-ordination number (MS₆) is more often to be observed in the sulpho salts than in the oxygen salts. This is probably due, in part at any rate, to the method of preparation of the sulpho salts, for they are prepared by melting the sulphide with an excess of alkali sulphide.

(g) Polysulphides.

Combinations of several sulphur atoms are able to act as divalent electronegative radicles. Compounds of this type are called polysulphides. With the exception of trisulphides, the existence of which is at present doubtful, a series of such sulphides, up to hexasulphides, is known, e.g.

K2S, K2SS, K2SS3, K2SS4

In the pentasulphide group Schiff¹ has prepared the zinc and cadmium compounds, ZnS₅, and CdS₅; Hofmann and Höchtlen the thallium salt, Tl₂S₅; Badroux² the copper compound, Cu₂S₅; and Blitz and Wilke-Dörpert³ the rhubidium and cæsium compounds. Jörgensen some time ago prepared a pentasulphide of a metal ammonium compound:

$$\left[\operatorname{Cr}^{\operatorname{Cl}}_{(\operatorname{NH}_3)_5} \right] \operatorname{S}_5 \cdot \left(\operatorname{Cr}^{\operatorname{Cl}}_{(\operatorname{NH}_3)_5} \right) \operatorname{Cr}^{\operatorname{Cl}}_{(\operatorname{NH}_3)_5} \right) \operatorname{Cr}^{\operatorname{Cl}}_{(\operatorname{NH}_3)_5} \cdot \left(\operatorname{Cr}^{\operatorname{Cl}}_{(\operatorname{NH}_3)_5} \right) \operatorname{Cr}^{\operatorname{Cl}}_{(\operatorname{NH}_3)_5$$

and also a rhodosopentasulphide, in a well-characterized form.

The hexasulphide of Rösing, cuprohexasulphide Cu₂S₆, is also of importance.

The constitution of polysulphides has been much discussed, but the most probable view of their constitution is that put forward by Drechsel, viz. that polysulphides are constituted similarly to the oxygen acids of sulphur, and hence pentasulphides are strictly comparable to sulphates:

$$\mathbb{K}_{2}\begin{bmatrix} \mathbf{O} \mathbf{S}_{\mathbf{O}}^{\mathbf{O}} \end{bmatrix}$$
 and $\mathbb{K}_{2}\begin{bmatrix} \mathbf{S} \mathbf{S}_{\mathbf{S}}^{\mathbf{S}} \end{bmatrix}$

The easy separation of sulphur from polysulphides of hydrogen does not militate in any way against this conception, for it is well known that sulphur is easily split off from the thiosulphates.

It is noteworthy that polysulphides can take part in the formation of sulpho salts, thus producing very peculiar compounds, as may be seen from the following, which were prepared by Hoffmann and Höchtlen:

AuS₃NH₄ Gold ammonium polysulphide

 $Ir(S_5NH_4)_3$ Iridium ammonium tripentasulphide

 $\mathrm{SPd}^{\mathrm{S_5NH_4}}_{\mathrm{S_5NH_4}}$

Paladium ammoniumdipenta-sulphide H₄NO₃S₂. Bi(S₅NH₄)₂ Bismuth ammonium polysulphidethiosulphate

$$S_5Pt$$
 $S_5NH_4 + 2H_2O$
 S_5NH_4

Platin ammonium triponta-sulphide

¹ Annalen, 115, 68 (1860).

² Compt. rend., 130, 1397 (1900).

Ber., 38, 128 (1905).

J. pr. Chem., (2) 20, 136 (1879).

⁵ Zeitsch. anorg. Chem., 25, 407 (1900).

⁶ Ber., 36, 3090 (1903).

Some very interesting compounds have been prepared from monovalent copper. They have the general formula CuS₄R, and behave as if they were salts of acid hydrogen cuprotetra-sulphide. The ammonium salt has been examined by Hofmann and Höchtlen, and the potassium, rubidium, and cæsium salts by Blitz and Herms.²

(h) Mixed Salts composed of Oxides, Sulphides, and Selenides.

The complete analogy which exists between double oxides, double sulphides, and double selenides renders it quite natural to expect that oxides, sulphides, and selenides can combine together. Such combinations result in the formation of compounds of the higher order, the acid radicle of which contains at the same time different elements of the oxygen group. Thus the following transition series between the oxides and sulphides is known in the case of arsenic:

$$[AsO_4]R_3, \ \left[As^S_{O_3}\right]R_3, \ \left[As^S_{O_2}\right]R_3, \ \left[As^S_{O_2}\right]R_3, \ \left[As^S_{O_3}\right]R_3, \ \left[AsS_4\right]R_3$$

The corresponding compounds of phosphorus provide such another series:

$$Na_3[PO_4] + 12H_2O$$
, $Na_3[P_{O_3}^S] + 12H_2O$, $Na_3[P_{O_2}^S] + 11H_2O$, $Na_3[P_{O_3}^S] + 10H_2O$, $Na_3[PS_4] + 8H_2O$

Molybdenum gives rise to an analogous series:

$$Na_{2}[MoO_{4}], Na_{2}[Mo_{S}^{O_{3}}], K_{2}[Mo_{S_{2}}^{O_{2}}], (K_{2})Na_{2}[MoS_{4}]$$

Further, the following mixed salts are interesting:

$$\begin{split} & \operatorname{Na_3}\!\!\left[P^{\mathrm{O}}_{\mathrm{S}e_3}\right] + 10 \mathrm{H_2O}, \quad \operatorname{Na_3}\!\!\left[\mathrm{Sb}^{\mathrm{S}e_3}_{\mathrm{S}}\right] + 9 \mathrm{H_2O}, \quad \operatorname{Na_3}\!\!\left[V^{\mathrm{O}}_{\mathrm{S_3}}\right] + 3 \mathrm{H_2O}, \\ & \operatorname{Na_4}\!\!\left[V^{\mathrm{O}_2}_{2\mathrm{S}_5}\right]^1 \\ & \operatorname{Na_3}\!\!\left[\mathrm{As}^{\mathrm{O}_2}_{\mathrm{S}e}\right] + 10 \mathrm{H_2O},^2 \quad \operatorname{Na_3}\!\!\left[\mathrm{As}^{\mathrm{S}e}_{\mathrm{S}_3}\right] + 8 \mathrm{H_2O}^2 \\ & \operatorname{Na_3}\!\!\left[\mathrm{As}^{\mathrm{S}_2}_{\mathrm{S}e_2}\right] + 9 \mathrm{H_2O},^2 \quad \operatorname{Na_3}\!\!\left[\mathrm{As}^{\mathrm{S}}_{\mathrm{S}e_3}\right] + 9 \mathrm{H_2O}^2 \end{split}$$

¹ Locke, Amer. Chem. J., 20, 373 (1898).

² Messinger, Ber., 30, 797 (1897).

Of other mixed salts the following may be noted:

 $3K_2S \cdot As_2Se_5 + 12H_2O$, $3Na_2S \cdot 3Na_2O \cdot 2As_2O_5 + 50H_2O$, $2K_2S \cdot P_2S_3 + 5H_2O$

 $\begin{array}{lll} {\bf Na_6As_2S_3SeO_4 + 20H_2O,} & {\bf Na_6As_2S_3Se_2O_3 + 2H_2O,} & {\bf Na_6As_2S_7Se} \\ & + 16H_2O, & {\bf Na_9As_3S_2Se_3O_8 + 36H_2O,} & {\bf Na_6As_2S_2SeO_5 + 24H_2O,} \\ & {\bf Na_6As_2S_5Se_3 + 16H_2O.^1} \end{array}$

¹ Messinger, Ber., 30, 797 (1897).

The thiosulphates belong to these mixed salts, for they are to be considered as members of the transition series between the sulphates and the pentasulphides:

$$R(SO_4)_2 R_2(S_{O_3}^S) R_2(SS_4)$$

The mixed salts which contain sulphur are particularly noticeable for their tendency to form complex salts, especially with sulphides which are not decomposed with water. This is very strikingly exhibited by the thiosulphates, and it is to this property that the solubility of silver chloride in alkaline thiosulphates is due. The complex AgS. SO₃Me is produced by this reaction, and is remarkable for its sweet taste. The sweet taste of AgS. SO₃NH₄ can be perceived even at a dilution of 1 in 320,000. The solubility of HgO in sodium thiosulphate with the consequent liberation of NaOH is to be ascribed to the formation of a complex,

which also has got a sweet metallic taste.

The ammonium salt:

takes up three further molecules of ammonium thiosulphate, forming a still more complicated compound.

The complex thiosulphates of bismuth which have been examined by Hauser are very interesting. They have the general formula—

$$S \cdot SO_3R$$

BiS · SO_3R
S · SO_3R

and the sodium, potassium, rubidium, cæsium, and barium salts have been prepared.

The composition of the copper alkaline thiosulphates is still more complicated, and up to the present satisfactory formulæ have not been found for them.

(i) Complex Oxygen Salts.

1. General.

From the fact that the cyano and thiocyanato salts are analogous to the halogeno salts, it follows that groups such as cyanogen take part in the formation of complex radicles in a similar way to elementary atoms (O, N, Cl, etc.). It is therefore natural to expect that simple oxygen salts likewise can take part in the formation of still more complex compounds. In such cases the radicles (NO₃), (NO₂), (SO₄), (SO₃), (CO₃), (C₂O₄), etc., would play the same rôle that oxygen, halogen, etc., play in the double oxides, double halides, etc. Experiment has shown this to be true, and the number and variety of the compounds which are thus produced are very great. Nitrates combine to form nitrato salts, sulphates yield sulphato salts, etc.

Such complex salts quite often behave as double salts, i.e. in aqueous solution they exhibit the reactions of their components. This is, for example, in the nitrato salts, ascribed to the hydrolyzing action of water.

The behaviour of the sulphates is more satisfactory, for the complexes they form are more stable. This behaviour is fore-shadowed in the behaviour of some simple sulphates, e.g. anhydrous chromium sulphate, which displays little tendency towards electrolytic dissociation. Carbonates and oxalates have a still greater capacity for the formation of complexes, so that a very great number of stable complex carbonates and oxalates are known. In order to understand correctly the constitution of these complex salts, it must be borne in mind that in the sulphato, carbonato, and oxalato salts similar phenomena are to be seen as in the oxygen salts, i.e. compounds which have been formed in conformity with the laws governing, the formation of molecular compounds change their constitution and pass into ordinary valency compounds. This behaviour is due to the divalency of the oxygen radicles, SO₄, CO₃, C₂O₄, etc.

This analogy may be made clear by comparing the changes:

(a) Transformation of a double oxide—

$$0: \overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\circ}}}} : OH_2 \longrightarrow 0: S < \overset{\circ}{\overset{\circ}{\overset{\circ}{\circ}}} : S < \overset{\circ}{\overset{\circ}{\overset{\circ}{\circ}}} H$$

Molecular compound

Valency compound

(b) Transformation of a double oxalate—

$$C_{0,C_{2}}^{O_{4}C_{2}}Z_{r} : C_{2}^{C_{2}O_{4}K_{2}} \rightarrow K_{O_{2}C} : C_{O_{2}}^{CO_{2}} > Z_{r} < C_{O_{2}}^{CO_{2}} : C_{O_{2}K}^{CO_{2}K}$$

Molecular compound

Valency compound

Such a transformation is only rendered impossible when the number of basic components, added to the complex, exceed a certain limit. The following compounds prepared by Rosenheim illustrate such a case:

$$[Th(CO_3)_5]Na_6 + 12H_2O, [Th(CO_3)_5]K_6 + 10H_2O, [Th(CO_3)_5] (NH_4)_6$$

and $[Th(CO_3)_5]Tl_6$

The stability of the nitrito and sulfito salts affords a striking contrast to that of the nitrato and sulfato salts, for the former are very stable indeed. This exceptional stability is due to a special cause. As is well known, these acids and their salts are tautomeric, i.e. they can give rise to isomeric derivatives of the following formulæ:

The salts of the heavy and noble metals are constituted according to formulæ II. and IV., and these salts contain the metal in a non-ionogene condition. On the other hand, the salts of the alkalis usually have constitutions represented by formulæ I. and III. In both these cases the central nitrogen and sulphur atoms, because they are strongly unsaturated, have a large residue of affinity which can act in the form of auxiliary valencies, and thus the addition of the alkali salts to those of the heavy metals gives rise to particularly stable complex salts.

The following paragraphs set forth the individual peculiarities of the complex oxygen salts.

2. Nitrato Salts.

Nitrato salts are compounds resulting from the combination of two or more simple nitrates.

The group of isomorphous complex nitrates with the general formula:

$$[Me(NO_3)_6]_2Me_3 + 24H_2O$$

is very interesting, for these salts, as is well known, are of considerable importance in the separation of the rare earths. The following members of this particular group have been described:—

					Mg	Zn	Cd	Mn	Со	Ni
La					+3	+3	_	+1	+2	_
Ce Bi Nd					+7	+8	+5	+5	_	+6
Bi					+9	+9		-	+9	+9
Nd					+10		_	_	_	_
Sa					+11	_	_	_	_	-
Gd					+12	_	E	= 1	_	+13
Sa Gd Ta				. 1		_	_	-	-	-

From this table it is clear that the nitrato salts have the same type-formula as the halogeno salts. The formation of a nitrato salt therefore must be considered as due to the mutual saturation of an auxiliary valency on an oxygen of the NO₃ group and auxiliary valency on the central metallic atom. The formation of potassium barium nitrate consequently takes place according to the scheme:

$$\begin{array}{c|c}
NO_3\\NO_3\\NO_3\\NO_3
\end{array} + O\\
+ O\\
NO_3\\
NO_3\\
K
= \begin{bmatrix}
NO_3\\NO_3\\NO_3
\end{bmatrix} K\\
NO_3\\NO_3
\end{bmatrix} K$$

- 1 Damour and Deville, Jahresb., 15, 1858.
- ² Frerichs and Smiths, Annalen, 191, 358 (1878).
- 3 Holzmann, J. pr. Chem., 75, 350 (1858).
- 4 Damour and Deville, loc. cit.
- ⁵ Lange, J. pr. Chem., 82, 129 (1861); Ziesche, ibid., 107, 65 (1869).
- 6 Lange, loc. cit.; Urbain, Compt. rend., 140, 583 (1905).
- ⁷ Rammelsberg, Pogg. Ann., 108, 435 (1859).
- 8 Lange, loc. cit.
- 9 Urbain and Lacombe, Compt. rend., 137, 568 (1903).
- 10 Demarçay, ibid., 126, 900 (1898).
- 11 Demarçay, ibid., 130, 1185 (1900).
- 12 Demarçay, ibid., 131, 345 (1900).
- us Urbain, ibid., 140, 583 (1905).

The majority of the elements which form nitrato salts belong to both the last series of the natural system of the elements.\(^1\) In the cæsium series the first elements, Ba, La, Ce, Ne, Pr, and the last, Au, Hg, Tl, Pb, Bi, possess this property. Thorium\(^2\) in the next higher series also has this property.

Beyond these elements a few of the heavy and of the noble metals (Ni, Fe, Ag), and also magnesium, are able to form nitrato salts. Hydrogen possesses an enormous capacity for the formation of complexes in which the acid radicle is probably represented by $[H(NO_3)_x]$. This is also true of the acid nitrates of some cobaltiates. It is also possible that the acid nitrates of the alkali metals are formed by the addition of nitrate residues to the alkali; thus:

RbNO₃·5HNO₃ gives [Rb(NO₃)₆]H₅

Of all the known nitrato salts in no single instance is the limiting type of the complex radicle Me(NO₃)₆ exceeded. It is also of interest to note that the most stable nitrato salts are prepared from the trivalent elements; bismuth, gold, and the alkaline earths.

The number of elements which form nitrato salts is relatively small. This peculiarity is to be ascribed to different causes. In the first place, the formation of nitrato salts only seldom can take place, because the formation of the simple nitrates already has used up some of the auxiliary valencies which are most suited to complex formation, i.e. the strongest. As a result of this the linking together of the components in nitrato salts often is very weak. Again, almost all the simple nitrates undergo considerable dissociation in aqueous solution, and this naturally must lead to the splitting up of the nitrato salts into simple ions upon solution in water.

² Uranium, it is true, forms nitrato salts, but they belong to a mixed type, thus:

The author is here referring to his own system of the elements. See table facing page 6. [Translator's note.]

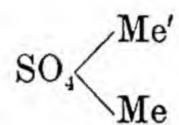
[[]UO₂(NO₃)₃]K,* [UO₂(NO₃)₃]Cs,* [UO₂(NO₃)₃]NH₄,* [UO₂(NO₃)₃]Tl †

* Meyer and Wenzel, Ber., 36, 4655 (1903); Sachs, Zeitsch. Kryst., 38, 496 (1903); Rimbach, Ber., 37, 461 (1904).

† Meyer and Wenzel, Ber., 36, 4655 (1903); Sachs, loc. cit., p. 496.

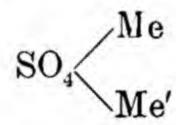
3. Double Sulphates and Sulphato Salts.

The number of double sulphates known is very great, and a classification, therefore, is desirable. This could be accomplished on the following lines. The simpler double sulphates are compounds in which both the hydrogen atoms of sulphuric acid have been replaced by different metals. They have, therefore, the general formula:



Sulphuric acid displays a great tendency towards the formation of such unsymmetrical salts, and this is probably due to a more effective saturation than would be the case were symmetrical salts formed.

The simple double-sulphates of the formula



may be divided into two sub-groups, according as one or both of the metallic atoms have ionogene properties:

$$\frac{Me}{Me'}SO_4 = \dot{Me} + \dot{Me'} + \dot{\overline{SO}}_4$$
 and $\frac{Me}{Me'}SO_4 = \dot{Me} + Me'SO_4$

In the former instance we have the ordinary double sulphate, and in the latter the complex sulphate. To this first group the alums and double sulphates belong:

$$[Me(OH_2)_{12}](SO_4)_2Me \quad and \quad [Me(OH_2)_6](SO_4Me)_2$$

In the second group we find the chromium sulphates, probably many compounds formed by the union of the sulphates of the alkaline earths with the sulphates of the alkalis, e.g.

and iridium potassium sulphate,

$$Ir(So_4K)_3 + OH_2$$

This latter compound has been examined by Delépine, who showed that it gave no precipitate of barium sulphate when treated with

¹ Compt. rend., 142, 1525 (1906).

barium chloride, but a bluish-green precipitate which contained iridium.

There is still a third sub-group to be mentioned. The members of this group are formed according to the ordinary laws governing the formation of co-ordination compounds. To this class belong such compounds as

$$Th(SO_4)_2 + 4SO_4K_2$$

its constitution doubtless being expressed by the formulæ:

$$\begin{array}{c} KO_3SO \\ KO_3SO \\ KO_3SO \\ KO_3SO \\ KO_3SO \\ \end{array} \begin{array}{c} Th \cdot OSO_3K_2 \\ OSO_3K_2 \\ OSO_3K_2 \\ \end{array} \begin{array}{c} OSO_3K_2 \\ OSO_3K_2 \\ OSO_3K_2 \\ \end{array} \\ \begin{array}{c} OSO_3K_2 \\ OSO_3K_2 \\ \end{array}$$

Cerium ammonium sulphate $Ce(SO_4)_2 + 3(NH_4)_2SO_4$ is also a member of this group. Unfortunately the behaviour of double sulphates in aqueous solution has scarcely received any attention, and hence an exhaustive theoretical treatment of these compounds is almost impossible. It is very desirable that these double sulphates be worked up on the lines suggested.

4. Double Oxalates and Oxalato Salts.

The residue of oxalic acid has also a tendency towards the formation of complex salts, for on collecting together the double oxalates and oxalate salts, it was found that about 300 compounds of these types have been prepared. Moreover, it can be shown that the formation of oxalate salts follow the same laws as other compounds of the higher order. The residue of oxalic acid can occupy two co-ordination positions; potassium chloroplateate thus corresponds to potassium oxalateplateate:

$$\begin{bmatrix} \text{Cl} & \text{Cl} \\ \text{Pt} & \text{Cl} \end{bmatrix}_{K_2} \quad \text{and} \quad \begin{bmatrix} \text{OCO} & \text{OCO} \\ \mid & \text{Pt} \\ \text{OCO} & \text{OCO} \end{bmatrix}_{K_2}$$

But it must be noted that this need not be always true, for under some conditions the oxalato residue takes up only one co-ordination position. This is probably the case in different oxalato salts of tetravalent metals, e.g.

Zr(OCOCOONH4)4,1 Th(OCOCOOK)4,2 U(OCOCOOK)4 3

The oxalato salts may be grouped together under certain types.

Venable and Baskerville, Am. Chem. Soc., 19, 13 (1897).

² Cleve, Bull. Soc. Chim., 21, 122 (1874).

Rammelsberg, Beilstein, Handb. org. Chem., p. 664.

Divalent metals yield salts of the type

$$\begin{bmatrix} \text{OCO} & \text{OCO} \\ \mid & \text{Me} & \mid \\ \text{OCO} & \text{OCO} \end{bmatrix} R_2$$

The following list affords illustrations of this type:

	Li	Na	K	NH ₄
$Mn(C_2O_4)_2R_2$	-	_	2H ₂ O 8	2H ₂ O 8
$\mathrm{Fe}(\mathrm{C_2O_4})_2\mathrm{R_2}$		_	${ 1 H_2^{O 9} \choose 2 H_2^{O 8} }$	3H ₂ O 9
$Co(C_2O_4)_2R_2$	_	_	6H ₂ O 1	_
$Ni(C_2O_4)_2R_2$		_	6H ₂ O 1	.
$\mathrm{Pd}(\mathrm{C_2O_4})_2\mathrm{R_2}$	_	-	3H ₂ O 10	${2 m H_{2}O^{18} \over 3 m H_{2}O}$
$\mathrm{Pt}(\mathrm{C_2O_4})_2\mathrm{R_2}$	-	${H_2O \atop 5H_2O \atop 4}$	2H ₂ O 11	2H ₂ O 19
$\mathrm{Cu}(\mathrm{C_2O_4})_2\mathrm{R}_2$	2H ₂ O ²	2H2O5	${2 m H_{2}O^{5} \choose 4 m H_{2}O^{12}}$	$2\mathrm{H}_2\mathrm{O}^{20}$
$Be(C_2O_4)_2R_2$	_	1H ₂ O 6	0H ₂ O 13	0H ₂ O 13
$Mg(C_2O_4)_2R_2$	_	_	6H ₂ O 14	_
$Zn(C_2O_4)_{\alpha}R_{\alpha}$	=	_	4H ₂ O 15	3H ₂ O 13
$Cd(C_2O_4)_2R_2$		2H ₂ O ⁷	2H ₂ O 7	
$\mathrm{Cd}(\mathrm{C_2O_4})_2^{\prime}\mathrm{R_2} \ \mathrm{Hg}(\mathrm{C_2O_4})_2^{\prime}\mathrm{R_2}$	-	_	2H ₂ O ⁸	2H ₂ O 8
$Sn(C_2O_4)_2R_2$; -	-	1H ₂ O 16	${{1 m H_{2}O}^{16}} \atop {3 m H_{2}O}^{16}$
$Pb(C_2O_2)R_2$	_	_	21H ₂ O 17	

- ¹ Rammelsberg, Beilstein, Handb. org. Chem., p. 664.
- ² Troost, Jahresb., 141 (1857).
- ³ Souchay and Lenssen, Annalen, 105, 256; Söderbaum, Bull. Soc. Chim., 45, 188 (1886).

 ⁴ Söderbaum, ibid.
 - ⁵ Vogel, Beilstein, Handb. org. Chem., 1, 646.
 - ⁶ Rosenheim and Woge, Zeitsch. anorg. Chem., 15, 286 (1897).
 - ⁷ Souchay and Lenssen, Annalen, 99, 31 (1856).
 - ⁸ Beilstein, Handb., 1, 644.
 - ⁹ Eder and Valenta, Monatsh., 1, 763 (1880).
 - 10 Vézes, Bull. Soc. Chim., (3) 21, 172 (1899).
 - 11 Vézes, ibid., (3) 19, 875; Söderbaum, ibid., 45, 188 (1886).
 - 12 Vogel and Rammelsberg, Beilstein, Handb. org. Chem., 1, 646.
- 13 Shadwell, Jahresb., 681 (1881); cf. Debray, Jahresb., 360, (1855); 295 (1857).
 - 14 Lenssen and Souchay, Beilstein, Handb. org. Chem., 1, 642.
 - 15 Kayser, Beilstein, ibid.
- Hausmann and Löwenthal, Annalen, 89, 104; Rammelsberg, Jahresb.,
 465 (1855).
 - 18 Kane, Beilstein, Handb. org. Chem., 1, 645.
- 19 Söderbaum, Bull. Soc. Chim., 45, 188; cf. Beilstein, Handb. org. Chem.,
- 1, 645.
 20 Graham, Annalen, 29, 8; Rammelsberg, Beilstein, Handb. org. Chem., 1, 646.

Trivalent elements yield oxalato salts of two chief types:

 $[Me(C_2O_4)_3]R_3$ and $[Me(C_2O_4)_2]R$

The following tables illustrate both types:—

(a) COMPOUNDS [$Me(C_2O_4)_3$] R_3 .

	Na	K	NH4
Vd(C2O4)3R3		3H ₂ O 8	3H ₂ O 8
$Cr(C_2O_4)_3R_3$	4½H ₂ O 1	3H ₂ O 9	3H ₂ O 19
$Mn(C_2O_4)_3R_3$	∫4½H2O2)	3H ₂ O 10	(217 0 11
$Fe(C_2O_4)_3R_3$	$\left\{5\frac{1}{2}H_{2}O^{3}\right\}$	$3\mathrm{H}_2\mathrm{O}^{11}$	${3 m H_{2}O^{11}} \over 4 m H_{2}O^{3}$
Co(C ₂ O ₄) ₃ R ₃	_	$3 H_2 O^{12}$	3H ₂ O 20
$Rh(C_2O_4)_3R_3$	6H ₂ O 4	4½H ₂ O 13	4½H ₂ O4
$Al(C_2O_4)_3R_3$	41H2O 5	${2\frac{1}{2}H_{2}O^{14} \choose 3H_{2}O^{15}}$	23H2O 5
$As(C_2O_4)_3R_3$		3H ₂ O 16	_
	(4177.06)	(3H ₂ O 6)	144
$Sb(C_2O_4)_3R_3$	$\left\{egin{matrix} 4rac{1}{2}H_{2}O^{6} \ 5H_{2}O^{7} \end{smallmatrix} ight\}$	$\left\{ egin{array}{c} 12 H_2 O^{16} \ 8 H_2 O^{17} \end{array} \right\}$	$\begin{cases} 2H_2O^{16} \\ 11H_1O^{18} \end{cases}$
	(0220)	4H ₂ O 18	$1_{\frac{1}{2}}H_{2}O^{18}$
$Bi(C_2O_4)_3R_3$	_		5H ₂ O ²¹

- 1 Mitscherlich, Rammelsberg and Schabus, Jahresb., 393 (1854); Rosenheim and Cohn, Zeitsch. anorg. Chem., 11, 204 (1896).
- ² Mitscherlich, Rammelsberg and Schabus, Beilstein, Handb. org. Chem., 1, 644.
 - ³ Eder and Valenta, Monatsh., 1, 763 (1880).
 - ⁴ Leidié, Ann. chim., (6) 17, 309 (1889).
 - ⁵ Rosenheim and Cohn, Zeitsch. anorg. Chem., 11, 182 (1896).
- ⁶ Svenssen, Ber., 3, 314 (1870); Rosenheim, Zeitsch. anorg. Chem., 20, 290 (1899).
- ⁷ Rammelsberg, Jahresb., 463 (1855); Souchay and Lenssen, Annalen, 105, 255 (1858).
 - * Piccini and Brizzi, Zeitsch. anorg. Chem., 19, 400 (1899).
 - ⁹ Croft, Berz. Jahresb., 23, 225 (1844).
- 10 Souchay and Lenssen, Annalen, 105, 254 (1858); Kehrmann, Ber., 20, 1595 (1887).
 - 11 Rammelsberg, Schabus and Bussy, Beilstein, Handb. org. Chem., 1, 644.
 - 12 Sörensen, Zeitsch. anorg. Chem., 11, 5 (1896).
 - 13 Dufet, Ann. chim., (6) 17, 307 (1889).
 - 11 Rosenheim and Cohn, Zeitsch. anorg. Chem., 11, 182 (1896).
 - 15 Kehrmann and Pickersgill, ibid., 4, 134 (1893).
 - 16 Souchay and Lenssen, Annalen, 105, 225 (1858).
 - 17 Wagner, Ber., 22, ref. 288 (1889).
 - 18 Rosenheim, Zeitsch. anorg. Chem., 20, 290 (1899).
- 19 Mitscherlich and Rammelsberg, Beilstein, Handb, org. Chem., 1, 643; Rosenheim and Cohn, Zeitsch. anorg. Chem., 11, 204 (1896).
 - 20 Marschall, Trans., 59, 769 (1891).
 - ²¹ Rosenheim, Zeitsch. anorg. Chem., 20, 305 (1899).

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Compare these salts with the halogeno salts of the type $(MeX_6)R_3$.*

(b)	COMPOUNDS	OF THE TYPE	[Me(C ₂ O ₄) ₂]R.
()	COLUTE	OF THE TIPE	1116(0001)2 IV.

	Na	K	NH ₄
Sa(C ₂ O ₄) ₂ R		2½H ₂ O ²	
$\operatorname{Er}(\mathrm{C}_2\mathrm{O}_4)_2\mathrm{R}$		$\frac{1}{2}H_2\tilde{O}^3$	
$Y(C_2O_4)_2R$	-	12H2O4	_
$Cr(C_2O_4)_2R$		${6 m H_{2}O m 5} \atop 5 m H_{2}O m 6}$	4H ₂ O 12
$Fe(C_2O_4)_2R$		$2\frac{1}{2}H_{2}O^{7}$	
$Al(C_2O_4)_2R$	51H2O1	3 H ₂ O 1	2½H,O1
$Tl(C_2O_4)_2R$		3H ₂ Õ 8	2½H ₂ O ¹³ 2H ₂ O ⁶
$Sb(C_2O_4)_2R$	_	$\left\{ egin{matrix} rac{1}{2} H_2 O & 10 \\ 1 H_2 O & 10 \end{smallmatrix} ight\}$	${5 m H_{2}O^{0} \choose 6 m H_{2}O^{10}}$
$\mathrm{Bi}(\mathrm{C_2O_4})_2\mathrm{R}$		${1 H_2O \atop 5 H_2O \atop 11}$	_

- ¹ Rosenheim and Cohn, Zeitsch. anorg. Chem., 11, 182 (1896).
- ² Cleve, Bull. Soc. Chim., 43, 171 (1885).
- 3 Cleve and Hoeglund, Beilstein, Handb. org. Chem., 1, 643.
- 4 Cleve and Hoeglund, Bull. Soc. Chim., 18, 294 (1872).
- ⁵ Croft and Berzelius, Jahresb., 23, 235; Rosenheim and Cohn, Zeitsch. anorg. Chem., 11, 204 (1896).
 - ⁶ Werner, Trans., 53, 405 (1888).
- ⁷ Eder and Valenta, Monatsh., 1, 763 (1880); Rosenheim and Cohn, Zeitsch. anorg. Chem., 11, 218 (1896).
 - 8 Rabe and Steinmetz, Zeitsch. anorg. Chem., 37, 88 (1903).
 - Svenssen, Ber., 3, 314 (1870).
 - 10 Rosenheim, Zeitsch. anorg. Chem., 20, 290 (1899).
 - 11 Ibid., 20, 305 (1899).
 - 12 Berlin, Beilstein, Handb. org. Chem., 1, 643.
 - 13 Rosenheim, Zeitsch. anorg. Chem., 21, 1 (1899).
- * The oxalate residue behaves when forming complex salts just like the bimolybdate residue Mo_2O_7 , for the latter forms a series of complex salts with trivalent elements with the general formula:

 $[Me(Mo_2O_7)_3]R_3$

as following list shows:

	Na	К	NH ₄
$[Al(Mo_2O_7)_3]R_3$ $[Cr(Mo_2O_7)_3]R_3$ $[Co(Mo_2O_7)_3]R_3$	11H ₂ O ² 10½H ₂ O ³	10H ₂ O ¹ 10H ₂ O ³ 7 ¹ / ₂ H ₂ O ⁴	10H ₂ O ¹ 10H ₂ O ³

- ¹ Struve, Annalen, 92, 267 (1854).
- ² Gentele, J. pr. Chem., 81, 414 (1860).
- ³ Struve, ibid., 61, 457 (1854).
- ⁴ Friedheim and Keller, Ber., 39, 4301 (1906).

Rubidium and cæsium salts of these different types of oxalato salts have not yet been prepared.

5. Double Sulphites and Sulphito Salts.

Sulphurous acid displays considerable capacity for the formation of stable complex salts in which the acid residue is linked by non-ionogene valencies to the noble and heavy metals. The following list of metals afford some idea of the type of metal which enter into these complex salts:—

To this group of metals, the members of which stand next one another in the periodic system, uranium has to be added. Up to the present, the mercury salts are the most accurately examined. Barth examined them and cleared up their complex constitution. He proved that in the salts

$$[Hg(SO_3)_2]Na_2 + H_2O$$
, $[Hg(SO_3)_2](NH_4)_2$ and $[Hg(SO_3)_2]K_2$

the mercury is not ionized, and consequently that the complex [Hg(SO₃)₂] behaves as a single acid radicle.

The reason for these salts not producing precipitates with phosphates, carbonates, ferro- and ferricyanides, is therefore clear. Péan de St. Giles was the first to record this peculiar behaviour.³

The compounds are to be considered, as Divers and Schimidzu have pointed out, as salts of a "mercury sulphonic acid."

Barth has also prepared the silver, strontium, and barium salts:

$$[Hg(SO_3)_2]Ag_2 + 2HO_2$$
, $[Hg(SO_3)_2]Sr + 2H_2O$, $[Hg(SO_3)_2]Ba + H_2O$

Other divalent metals give rise to sulphito salts, which are represented by the general formulæ

$$Me < SO_3R$$
 and $Me < SO_3R + 2MeSO_3$ SO_3R

1 Trans., 49, 533 (1886).

I.e. Author's system. [Translator's note.]

Zcitsch. physikal. Chem., 9, 176 (1892).
 Ann. Chim. Phys., (3) 36, 80 (1852).

Compounds of the latter type probably have the following constitutional formula:

$$[\mathrm{Me}(\mathrm{SO_3})_4]\mathrm{R}_4$$

The following compounds are known:1

The composition of the double sulphites of copper and silver is very complicated and obscure, for the results of different experiments lead to very different conclusions. Rosenheim 2 explains these divergent results by assuming that many of the substances described as compounds are in reality solid solutions of, for example, alkali sulphite in copper sulphite.

Gold forms two series of sulphito salts:

and those of palladium 5 and platinum 6 are also interesting:

$$[Pd(SO_3)_4]Na_6 + 2H_2O, [Pt(SO_3)_4]Na_6 + H_2O, \\ [Pt(SO_3)_4]K_6, [Pt(SO_3)_4](NH_4)_6 + 3H_2O, [Pt(SO_3)_3]Na_4 + 2H_2O$$

The salts correspond to the halogeno type [MeX₄]R₂, and hence it is to be assumed that the sulphite residue only occupies one coordination position.

Three more platinum salts are known:

$$Pt = SO_3Na + H_2O Pt = SO_3NH_4 + H_2O Pt = SO_3K + H_2O$$

The trivalent elements, cobalt, rhodium and iridium, yield sulphito salts of the general formula: [Me(SO₃)₃)]R₃, thus:

- ¹ Berglund, Ber., 7, 470 (1874).
- ² Zeitsch. anorg. Chem., 25, 78 (1900).
- 3 Hasse, Zeitsch. f. Chem., 12, 535 (1869).
- ⁴ Frémy, Ann. Chim. Phys., (3) 31, 485 (1851).
- ⁵ Wöhler, Annalen, 174, 200 (1875).
- 6 Litton and Schnedermann, Annalen, 42, 318 (1842); Peyronne, ibid., 51, 5 (1844); Liebig, ibid., 23, 23 (1837); Claus, Pogg. Ann., 28, 181 (1833).

$$\begin{split} &[\text{Co(SO}_3)_3]_2\text{Ba}_3,^1 \quad [\text{Co(SO}_3)_3]_2\text{Ca}_3,^1 \quad [\text{Co(SO}_3)_3]_2\text{Co}_3,^1 \quad [\text{Co(SO}_3)_3]\text{Ag}_3,^1 \\ &[\text{Rh(SO})_3]\text{K}_3 + 3\text{H}_2\text{O},^2 \quad [\text{Rh(SO}_3)_3]\text{Na}_3 + 2\text{H}_2\text{O},^2 \quad [\text{Ir(SO}_3)_3]\text{K}_3 \\ &+ 3\text{H}_2\text{O},^3 \quad [\text{Ir(SO}_3)_6]\text{Na}_3 + 4\text{H}_2\text{O},^3 \quad [\text{Ir(SO}_3)_3](\text{NH}_4)_3 + 1\frac{1}{2}\text{H}_2\text{O}^3 \end{split}$$

A great many sulphite salts containing different alkali metals are known. It should be noted that the isomerism between KSO₃Na and NaSO₃K, which Barth thought he proved to exist, has been denied by Fraps.⁴

(k) On Mixed Salts consisting of Oxides with Halides, Cyanides, etc.

Since it has been found practicable to combine oxides, sulphides, etc., with halides, cyanides, etc., we have therefore the possibility of forming many new classes of complex salts. Much is already known about such compounds, but their systematic investigation will require very extensive work.

To characterize these compounds a few examples of their manner of formation are given.

Just as basic oxides are taken up by chromium trioxides:

$$O C_r + OK_2 = O C_r \cdot OK_2 \rightarrow (CrO_4)K_2$$
 (potassium chromate)

so in like manner compounds are formed from halides and chromium trioxide:

$$\begin{array}{l}
O_{\text{Cr}}^{O} + \text{ClnH}_{4} = O_{\text{Cr}}^{O} \cdot \text{ClnH}_{4} \rightarrow \left[\text{Cr}_{\text{Cl}}^{O_{3}}\right] \text{NH}_{4} \\
O_{\text{Cr}}^{O} + \text{FnH}_{4} = O_{\text{Cr}}^{O} \cdot \text{FnH}_{4} \rightarrow \left[\text{Cr}_{\text{F}}^{O_{3}}\right] \text{NH}_{4}
\end{array}$$

In these compounds we have to deal with salts in which the complex acid residue contains halogen and oxygen. In a similar manner the formation and constitution of the following compounds are to be explained:—

¹ Berglund, Ber., 7, 469 (1874).

² Seubert and Kobbe, Ber., 23, 2558 (1890).

Birnbaum, Annalen, 136, 183 (1865).
 Amer. Chem. J., 32, 202 (1907).

1. Fluoxo-salts.

With reference to fluoxo-salts it is worthy of note that the elements which show the greatest tendency to form this class of salt are those which occupy neighbouring positions in the periodic systems, i.e.

The following list illustrates the fluoxo-salts of these elements.

$$\begin{bmatrix} \mathrm{Ti}_{F_6}^{O_2} \Big] R_2^{-1} & \left[\mathrm{Ti}_{F_6}^{O_2} \Big] R_2 + \mathrm{RF}^{-1} & \left[\mathrm{V}_{F_5}^{O} \right] R_2^{-2} & \left[\mathrm{V}_{F_4}^{O_2} \right] R_3^{-3} \\ \begin{bmatrix} \mathrm{V}_{F_4}^{O} \\ \mathrm{OH}_2 \end{bmatrix} R_2^{-4} & \left[\mathrm{Cr}_{F}^{O_3} \right] R_5 & \left[\mathrm{Nb}_{F_5}^{O} \right] R_2 + \mathrm{RF}^{-6} & \left[\mathrm{Nb}_{F_4}^{O} \right] R_2^{-7} \\ \begin{bmatrix} \mathrm{Mo}_{F_5}^{O} \Big] R_2^{-8} & \left[\mathrm{Mo}_{F_5}^{O} \right] R_2^{-9} & \left[\mathrm{Mo}_{F_5}^{O_3} \right] R_2^{-9} & \left[\mathrm{Ta}_{F_5}^{O} \right] R + \mathrm{RF}^{-10} \\ \begin{bmatrix} \mathrm{W}_{F_4}^{O_2} \right] R_2^{-11} & \left[\mathrm{W}_{F_4}^{O_2} \right] R_2^{-11} & \left[\mathrm{W}_{F_4}^{O_2} \right] R_2^{-11} \end{bmatrix}$$

- 1 Piccini, Rend. Acad. Lincei, 1885.
- ² Piccini, Ber., 21, 586 (1888).
- ³ Dammer, Lehrb., III., p. 714.
- ⁴ Baker, Ber., 11, 1722 (1878).
- ⁵ Werner, Zeitsch. anorg. Chem., 9, 407 (1895).
- ⁶ Baker, Trans., 35, 760 (1879).
- ⁷ Marchetti, Zeitsch. anorg. Chem., 10, 66 (1895).
- ⁸ Mauro, Gazz. chim., 19, 179 (1889).
- 9 Mauro, ibid., 18, 120 (1888); 19, 179 (1889); 20, 109 (1890).
- ¹⁰ Marignac, Ann. Chim. Phys., (4) 9, 268 (1866): Marchetti, Zeitsch. anorg. Chem., 10, 66 (1895).
 - 11 Marignac, Ann. Chim. Phys., (3) 69, 65 (1863).

Of the other elements which give well-characterized fluoxosalts, uranium, iodine and boron, deserve mention:

$$\begin{split} \left[U_{F_{5}}^{O_{2}}\right] & K_{3} \quad \left[U_{2F_{7}}^{O_{4}}\right] K_{3} \quad \left[U_{2F_{9}}^{O_{4}}\right] K_{5} \quad \left[U_{F_{3}}^{O_{2}}\right] Na + 2H_{2}O \text{ and } + 4H_{2}O \\ & \left[U_{F_{5}}^{O_{2}}\right] (NH_{4})_{3} \quad \left[U_{F_{5}}^{O_{2}}\right] Ba_{3} + 2H_{2}O^{1} \quad \left[I_{F_{2}}^{O_{2}}\right] K^{2} (Na, Rb, Cs, NH_{4}) \\ & B_{2}O_{3} (FK)_{2}^{3} \end{split}$$

- ¹ Bolton, Jahresb., 1866, p. 166; Smithells, Trans., 43, 125 (1883).
- ² Weinland and Lauenstein, Ber., 30, 866 (1897).
- ³ Schiff and Sestini, Annalen, 228, 72 (1884).

It seems to the author doubtful whether the fluoro-sulphates, dithionates, and phosphates which Wein and and Alfa 1 prepared are to be classed amongst the above compounds. For it would be very peculiar indeed if hydrofluoric acid were able to replace oxygen in phosphoric and sulphuric acids. It is not impossible that these compounds are hydrofluoric acid addition products of phosphates, sulphates, etc., e.g.

$$(PO_4)_{K}^{H_2} + H\dot{F}, (PO_4)_{Rb}^{H_2} + HF, (PO_4)_{Cs}^{H_2} + HF, K_2S_2O_6 + 2HF + H_2O, Rb_2S_2O_6 + 2HF + H_2O, Cs_2S_2O_6 + HF + H_2O, K_2SO_4 + KHSO_4 + 2HF, Rb_2SO_4 + RbHSO_4 + 2HF, Cs_2SO_4 + CsHSO_4 + 2HF.$$

2. Halogenoxo Salts with Other Halogens.

$$\begin{split} & \Big[Cr_{Cl_4}^O \Big] R^{\ 1} \quad \left[M_0 {\overset{O_2}{Cl_3}} \right] R^{\ 2} \quad \left[M_0 {\overset{O_2}{Cl_4}} \right] R_2^{\ 2} \quad \left[M_0 {\overset{O_6}{Cl_5}} \right] R^{\ 2} \quad \left[M_0 {\overset{O_{19}}{Cl_8}} \right] R^{\ 2} \\ & \quad \left[M_0 {\overset{O_3}{Cl_2}} \right] H_2^{\ 3} \quad \left[V_{Cl_3}^{O_2} \right] R_2^{\ 4} \quad \left[V_{Cl_6}^O \right] R_4^{\ 5} \quad \left[V_{Cl_4}^O \right] R_2^{\ 6} \quad \left[V_{Cl_4}^O \right] R^{\ 6} \\ & \quad \left[N_0 {\overset{O_1}{Cl_2}} \right] R^{\ 6} \quad \left[N_0 {\overset{O_1}{Cl_5}} \right] R_2^{\ 6} \quad \left[Ta_{Cl_5}^O \right] R_2^{\ 6} \quad \left[Ta_{2Cl_9}^{O_2} \right] R_3^{\ 6} \\ & \quad \left[Ta_{2Cl_8}^{O_3} \right] R_4^{\ 6} \end{split}$$

1 Weinland and Fridrich, Ber., 38, 3784 (1905).

² Weinland and Knöll, Ber., 37, 569 (1904); Zeitsch. anorg. Chem., 44, 81 (1905).

² Péchard, Compt. rend., 114, 173 (1892).

Ephraim, Zeitsch. anorg. Chem., 35, 71 (1903).

⁵ Koppel and Kaufmann, ibid., 45, 345 (1905).

Weinland and Storz, ibid., 54, 223 (1907).

$$\begin{bmatrix} Os_{Cl_{4}}^{O_{2}} R_{2}^{-1} & \left[Os_{Cl_{2}}^{O_{3}} \right] R_{2}^{-1} & \left[U_{Cl_{4}}^{O_{2}} \right] R_{2}^{-2} & \left[Mo_{Br_{4}}^{O} \right] R^{-3} & \left[Mo_{Br_{5}}^{O} \right] Cs_{2}^{-3} \\ & \left[Mo_{Br_{3}}^{O_{3}} \right] H_{3}^{-3} & \left[Nb_{Br_{4}}^{O} \right] R^{-4} & \left[Nb_{Br_{5}}^{O} \right] R_{2}^{-4} & \left[Os_{Br_{4}}^{O_{2}} \right] R_{2} \\ & \left[Os_{Br_{2}}^{O_{3}} \right] R_{2}^{-1} & \left[U_{Br_{4}}^{O_{2}} \right] R_{2}^{-5} & \left[Mo_{I}^{O_{3}} \right] H^{-3} \\ \end{bmatrix} H^{-3}$$

Wintrebert, Ann. Chim. Phys., (7) 28, 15 (1903).

² Berzelius, Pogg. Ann., 1, 366 (1824); Péligot, Annalen, 43, 279 (1842).

Weinland and Knöll, Zeitsch. anorg. Chem., 44, 81 (1905).

Weinland and Storz, ibid., 54, 223 (1907).

⁵ Berthelot, Ann. Chim. Phys., 44, 387 (1830).

¹ Weinland and Alfa, Zeitsch. anorg. Chem., 21, 43 (1899).

Attention may also be directed to some compounds which probably belong to the oxohalogeno salts:

3. Cyano and Thiocyano Salts.

Cyanides and thiocyanides form complex salts with oxides corresponding to halogenoxo salts. To this class belong the following compounds:

$$\begin{split} & \Big[Mo_{(\mathrm{SCN})_5}^{\mathrm{O}} \Big] R_5^{-1} \ \Big[V_{(\mathrm{SCN})_4}^{\mathrm{O}} \Big] R_2^{-2} \ \Big[V_{2\mathrm{C}\mathbf{y}_4}^{\mathrm{O}_7} \Big] K_8^{-3} \ \Big[V_{\mathrm{C}\mathbf{y}_4}^{\mathrm{O}} \Big] K_2 + 5 \mathrm{H}_2 \mathrm{O}^{-3} \\ & \Big[Mo_{\mathrm{C}\mathbf{y}_4}^{\mathrm{O}_2} \Big] K_4 + 10 \mathrm{H}_2 \mathrm{O}^{-4} \ \Big[Mo_{2} \frac{\mathrm{C}\mathbf{y}_6}{\mathrm{S}_3} \Big] K_6 + 5 \mathrm{H}_2 \mathrm{O}^{-4} \ \Big[Mo_{2} \frac{\mathrm{S}}{\mathrm{C}\mathbf{y}_6} \Big] K_4 \\ & + 4 \mathrm{H}_2 \mathrm{O}^{-4} \ \Big[Mo_{3} \frac{\mathrm{S}_4}{\mathrm{C}\mathbf{y}_8} \Big] K_5 + 7 \mathrm{H}_2 \mathrm{O}^{-4} \end{split}$$

- ¹ Rosenheim and Koss, Zeitsch. anorg. Chem., 49, 148 (1906).
- ² Koppel and Goldmann, ibid., 36, 281 (1903).
- ³ Petersen, ibid., 38, 342 (1904).
- ¹ K. v. der Heide and Hoffmann, ibid., 12, 275 (1896).

(1) Mixed Salts consisting of Halides, Cyanides, Oxides, etc., with Oxygen Salts.

Halides, cyanides, thiocyanides, nitrates, oxalates, nitrites, sulphites, etc., can combine together in the most varied manner, as Kohlschütter¹ in particular has recently shown. In this manner an immense variety of complex salts can be produced. It would lead us too far to discuss their individual peculiarities, but it ought to be noted that up to the present the behaviour of these compounds has received very little attention, in spite of the fact that in this branch of the subject valuable results are to be expected on isomeric phenomena, constitution ratios, etc., etc.

In order to give some idea of this type of compound the following list is appended:

$$\left[Pt_{(NO_2)_4}^{Cl_2}\right]R_2^{-1} \quad \left[Pt_{(NO_2)_4}^{Br_2}\right]R_2^{-1} \quad \left[Pt_{I_2}^{(NO_2)_2}\right]R_2^{-1} \quad \left[Ir_{(NO_2)_2}^{Cl_4}\right]R_3^{-2}$$

1 Vèzes, Compt. rend., 112, 616 (1891); 113, 696 (1891).

² Miolati and Gialdini, Atti R. Accad. d. Lincei, Rome, (5) 11, II. 151 (1902).

$$\begin{bmatrix} Cd_{2}^{Cl_{2}} \\ CQ_{2}^{CQ_{4}} \end{bmatrix} K_{4}^{1} & \begin{bmatrix} Cd_{4}^{Cl_{10}} \\ CQ_{2}^{CQ_{4}} \end{bmatrix} (NH_{4})_{8}^{1} & \begin{bmatrix} Hg_{2}^{Cl_{6}} \\ CQ_{2}^{CQ_{4}} \end{bmatrix} K_{4}^{1} \\ \begin{bmatrix} Os_{Cl_{5}}^{NO} \end{bmatrix} R_{2}^{2} & \begin{bmatrix} Os_{Br_{5}}^{NO} \end{bmatrix} R_{2}^{2} & \begin{bmatrix} Os_{I_{5}}^{NO} \end{bmatrix} R_{2}^{2} & \begin{bmatrix} VQ_{2}^{O_{2}} \\ V_{2}^{OQ_{4}} \\ SO_{4} \end{pmatrix}_{3} \end{bmatrix} R_{2}^{3} \\ \begin{bmatrix} V_{(SO_{4})_{2}}^{O_{2}} \end{bmatrix} R_{2}^{3} & \begin{bmatrix} V_{2}^{O_{2}} \\ CQ_{2}^{O_{4}} \\ V_{2}^{OQ_{4}} \end{bmatrix} R_{2}^{4} & \begin{bmatrix} UQ_{2}^{O_{2}} \\ UQ_{2}^{OQ_{4}} \\ V_{2}^{OQ_{4}} \end{bmatrix} R_{2}^{5} & \begin{bmatrix} VQ_{2}^{O_{2}} \\ VQ_{2}^{OQ_{4}} \\ VQ_{2}^{OQ_{4}} \end{bmatrix} R_{2}^{6} & \begin{bmatrix} MoQ_{3}^{O_{3}} \\ VQ_{2}^{OQ_{4}} \\ VQ_{2}^{OQ_{4}} \end{bmatrix} R_{2}^{7} \\ \begin{bmatrix} Nb(C_{2}O_{4})_{3} \end{bmatrix} R_{3}^{8} & \begin{bmatrix} Os_{(NO_{2})_{2}}^{O_{3}} \end{bmatrix} R_{2}^{2} & \begin{bmatrix} Os_{(NO_{2})_{4}}^{O_{2}} \end{bmatrix} R_{2}^{2} \\ \begin{bmatrix} Os_{(C_{2}O_{4})_{2}}^{OQ_{4}} \end{bmatrix} K_{2}^{9} & \begin{bmatrix} Os_{(C_{2}O_{4})}^{O_{3}} \end{bmatrix} R_{2}^{10} & \begin{bmatrix} Pt_{(C_{2}O_{4})}^{OQ_{2}} \end{bmatrix} R_{2}^{11} \\ \begin{bmatrix} Cd_{2}^{(C_{2}O_{4})_{3}} \\ VQ_{2}^{OQ_{4}} \end{bmatrix} K_{4}^{1} & \end{bmatrix}$$

¹ Kohlschütter, Ber., 35, 483 (1902).

² Wintrebert, Ann. Chim. Phys., (7) 28, 15 (1903).

³ Koppel and Behrent, Zeitsch. anorg. Chem., 35, 154 (1903).

⁴ Koppel and Goldmann, ibid., 36, 281 (1903).

⁵ Rimbach, Ber., 37, 461 (1904).

6 Rosenheim and Frank, ibid., 38, 812 (1905).

⁷ Grossmann and Krämer, Zeitsch. anorg. Chem., 41, 43 (1904).

8 Russ, ibid., 31, 42 (1902).

Vèzes and Wintrebert, Bull. Soc. Chim., (3) 27, 569 (1902).

10 Vèzes, ibid., (3) 29, 83 (1903).

11 Vèzes, ibid., (3) 27, 930 (1902).

That sulphites take part in the formation of mixed salts in a similar way is to be seen in the interesting series of platinum salts:

$$\left[Pt_{\mathrm{Cl}_2}^{(\mathrm{SO}_3)_2} \right] (\mathrm{NH_4})_4 \quad \left[Pt_{\mathrm{Cl}_3}^{\mathrm{SO}_3} \right] K_3 \quad \left[Pt_{\mathrm{Cl}_3}^{\mathrm{SO}_3} \right]_{(\mathrm{NH}_4)_2}^{\mathrm{H}} \quad \left[Pt_{\mathrm{Cl}}^{(\mathrm{SO}_3)_2} \right] K_3$$

Iridium also yields such another series:

$$\left[Ir_{Cl_3}^{(SO_3)_2}\right]K_4$$
 $\left[Ir_{Cl_5}^{SO_3}\right]K_4$ $\left[Ir_{Cl}^{(SO_3)_3}\right]K_4$ $\left[Ir_{Cl_4}^{SO_3}\right]K_3^2$

The complex salts of monovalent copper and silver which Rosenheim and Steinhauser³ described, are of very great importance. They crystallize very perfectly, and their composition shows them to be complexes formed from copper or silver monohalide or thiocyanide with ammonium thiosulphate; but the most important

¹ Birnbaum, Annalen, 152, 137 (1869); 159, 116 (1871).

² Claus, ibid., 63, 337 (1847); ibid., 107, 137 (1858); J. pr. Chem., 42, 356 (1847).

3 Zeitsch. anorg. Chem., 25, 103 (1900).

point is that the co-ordination number of these monovalent elements is six, e.g.

$$\begin{bmatrix} Ag_{(S_2O_3)_4}^{Cl_2} \end{bmatrix} (NH_4)_9 & \begin{bmatrix} Ag_{(S_2O_3)_4}^{Br_2} \end{bmatrix} (NH_4)_9 & \begin{bmatrix} Ag_{(S_2O_3)_4}^{I_2} \end{bmatrix} (NH_4)_9 \\ \begin{bmatrix} Ag_{(S_2O_3)_4}^{(SCN)_2} \end{bmatrix} (NH_4)_9 & \begin{bmatrix} Cu_{(S_2O_3)_4}^{Cl_2} \end{bmatrix} (NH_4)_9 & \begin{bmatrix} Cu_{(S_2O_3)_4}^{Br_2} \end{bmatrix} (NH_4)_9 \\ \begin{bmatrix} Cu_{(S_2O_3)_4}^{I_2} \end{bmatrix} (NH_4)_9 & \begin{bmatrix} Cu_{(S_2O_3)_4}^{(SCN)_2} \end{bmatrix} (NH_4)_9 \\ \end{bmatrix}$$

Finally, the compounds of the Wagnerite group belong to mixed salts described above, i.e.

$$MgO_3PO$$
 $Mg < MgF_2$
 MgO_3PO

(m) Hydrates formed by Addition.

1. The Metallic Hydroxides.

When water is taken up by a metallic oxide, a double oxide results, and this latter compound very often undergoes a further change which is brought about by the divalency of oxygen and the mobility of the hydrogen atom, and which results in the production of a metallic hydroxide. These changes may be expressed by the following equations:

$$MeO + OH_2 = OMe \cdot OH_2 \rightarrow Me < OH$$

Some of these hydroxides have the additional property of being able to take up other metallic hydroxides, thus producing salts which will be called hydroxo salts, and are comparable to the simple oxo salts, thus:

In the acid radicles of the hydroxo salts the hydroxyl groups play the same part as oxygen in the ordinary oxygen salts, or halogen in the halogeno salts. As a matter of fact, a complete analogy exists between halogeno and hydroxo salts, as we will proceed to show. Thus plate hydroxide corresponds to plate chloride:

Plate hydroxide combines with two molecules of alkali hydroxide; a reaction which is completely analogous to the union of plate chloride with two molecules of potassium chloride:

$$HO : Pt : OH = \begin{bmatrix} OH & OH \\ HO : OH \\ Pt : OH \end{bmatrix} K_{2}$$

$$CI : Pt : CI + 2CIK = \begin{bmatrix} CI & CI \\ CI : CI \\ CI : CI \end{bmatrix} K_{2}$$

Other metallic hydroxides behave quite similarly to plate hydroxide, e.g. stanne hydroxide and plumbe hydroxide:

$$(HO)_4Sn + 2KOH = [Sn(OH)_6]K_2$$

 $(HO)_4Pb + 2KOH = [Pb(OH)_6]K_2$

The complete analogy which exists between these three metallic hydroxides has been demonstrated in the beautiful researches of Bellucci and Parrayano.1

Salt-formation with these metallic hydroxides does not take place according to the theory of amphoteric ions (i.e. by the substitution of hydroxyl hydrogen for metal), as up to the present believed to be the case, but rather by the addition of basic hydroxides to the central metallic atom of the metallic hydroxide. It is a characteristic of these hydroxo salts that the hydrogen of the hydroxyl group when acted upon by a base cannot be replaced by the metallic atom. This behaviour constitutes the difference between these salts and the ordinary oxygen salts (oxo salts), for in the latter hydrogen has acidic properties. The hydrates of the metallic hydroxides

¹ Atti Acad. R. d. Lincei, Roma, (5) 14, I. 378 (1905); Gazz. Chim., 85, 500 (1905).

(HO)₄Pt(OH₂)₂, (HO)₄Sn(OH₂)₂, (HO)₄Pb(OH₂)₂, are to be considered as the acids of these hydroxo salts. It should be noted, however, that in most cases these hydrates are not stable in the free state, but decompose into metallic hydroxide and water. In this respect they are completely analogous to carbon dioxide and such compounds, a fact which would have to be remembered in a general treatment of the acids.

At present the number of hydroxo salts is small, but research in this direction ought to add greatly to the number. In this connection, it is certain that Senderens' salt is produced from an acid of antimony which is as yet unknown.

The solubility of the hydroxides of zinc, aluminium, etc., in alkali is to be referred to the formation of hydroxo salts of this type. The changes which take place in such cases are quite analogous to the solution of mercuric iodide in potassium iodide:

$$I_2Hg + IK = [HgI_3]K$$

$$(HO)_2Zn + KOH = [Zn(OH)_3]K$$

This conception is justified in the case of aluminium for a whole series of salts, the existence of which is predicted by the theory, can be isolated.

The following types of salts are to be expected:

And since the following salts are described in the literature:2

 $2Al(OH)_3$. $Ba(OH)_2 + H_2O$ and $2H_2O$, $Al(OH)_3$. KOH, $Al(OH)_3$. NaOH, $Al(OH)_3$. $2TlOH + H_2O$, $Al(OH)_3$. $Ca(OH)_2 + H_2O$, $Al(OH)_3$. $Ba(OH)_2$, $2Al(OH)_3$. $3Sr(OH)_2$, $2Al(OH)_3$. $3Sr(OH)_2$, $2Al(OH)_3$.

we have therefore examples of every possible type. The zincoates have been much less investigated. The following compounds have been described: 3

 $Zn(OH)_2$. NaOH + $2\frac{1}{2}H_2O$, $2Zn(OH)_2 + Ca(OH)_2 + 4H_2O$, $2Zn(OH)_2$. Sr $(OH)_2 + 7H_2O$, $2Zn(OH)_2$. Ba $(OH)_2 + 7H_2O$, $3Zn(OH)_2$. 4NaOH + $13H_2O$

The auriates also belong to the hydroxo salts; potassium

¹ Bull. Soc. Chim., (3) 21, 47 (1899).

² Beckmann, J. pr. Chem., 26, 385 (1882); Allen and Rogers, Amer. Chem. J., 24, 304 (1900); Hawley, J. Amer. Soc., 29, 300 (1907).

³ Comey and Jackson, Amer. Chem. J., 11, 145 (1889); Bertrand, Compt. rend., 115, 939 (1892).

auriate has the following composition: $KAu(OH)_4 + H_2O_7$ and corresponds to potassium chloroauriate $KAuCl_6 + H_2O$.

The examination of the hydroxo salts of aluminium and zinc shows that the salts formed with the divalent metals are much more stable than those formed with monovalent, for the aluminiates and the zincoates of the metals of the alkaline earths are much more stable than the corresponding alkali salts. Related to this stability is the fact that the divalent metals form rings which are very stable indeed, e.g.

The importance of these rings will be made clear when, in the following paragraph, we are discussing basic metallic salts.

2. Hydrates formed by Addition to Salts.

In order to simplify the treatment of this class of hydrates, it is proposed to discuss first those hydrates which are formed by the addition of water to metallic halides. In the general part of this book we have discussed already the constitution of addition compounds of this description, choosing the hydrate of platinum chloride as our example: Cl₄Pt(OH₂)₂.

We saw that the compound has the following constitution:

$$\begin{array}{c|c} Cl & Cl \\ \hline \\ Pt < OH_2 \\ \hline \\ Cl & Cl \end{array}$$

and that it is a dibasic acid:

$$\left(\operatorname{Pt^{\operatorname{Cl}_4}_{(\operatorname{OH})_2}}\right)$$
 H_2

The great electrolytic dissociation of water in such addition compounds can be ascribed to the influence of the complex, but it can also have another cause. It might be due to a type of tautomerism similar to that which has been proved in organic

¹ Frémy, Ann. Chim. Phys., (3) 31, 438 (1851).

chemistry to exist between acids and pseudo acids. The hydrate of platinum chloride could be tautomeric in the following sense:

$$\begin{array}{ccc}
OH_{2} & & & OH \\
PtCl_{4} & \rightarrow & Cl_{2}Pt < & ClH \\
OH_{2} & & OH
\end{array}$$

The second formula contains the hydrogen as a component of CIII, and therefore explains the acid properties of the compound in a satisfactory way. Such a conception brings these compounds into very close relationship with the ordinary oxygen acids, as may be seen from the following equations:

$$\begin{array}{c}
O \\
OS \\
OS \\
OH
\end{array}$$

$$OH_2 = OS \\
OH_2 \\
OH_2 \\
OH$$

All halides which are undissociated in aqueous solution behave like the chlorides of gold and platinum. This, for example, has been shown to be true in the case of platinum iodide, for from the hydrate: $Pt_{(OH_2)_2}^{I_4}$ Bellucci¹ has been able to prepare the silver, thallium, mercury, and basic lead salts.

These addition hydrates take up a position intermediate between the halogeno and hydroxo salts. Thus in the theoretical part it has been shown that in the salts of tetravalent platinum, with only one exception, all the compounds intermediate between platinic acid $[Pt(OH)_6]H_2$ and hexachloroplatinic acid $[PtCl_6]H_2$ have been prepared and characterized by salts. Again Miolati and Pendini were able to show that Nilson's decomposition product $(PtCl_3)H + xH_2O$ of chloroplato acid, $[PtCl_4]H_2$, is a dibasic acid and has the formula $[Pt_{OH}^{Cl_3}]H_2$. They were able also to prepare its silver and lead salts. Biilmann and Andersen have prepared from the corresponding bromo acid, a compound which is to be considered as the allyl ester of the potassium salt:

$$\left(\mathbf{Pt}_{\mathbf{OH}}^{\mathbf{Br_3}}\right)_{\mathbf{C_3H_5}}^{\mathbf{K}}$$

¹ Bellucci, Atti R. Acad. dei Lincei, Roma, (5) 11, I.8; II. 241, 271 (1902).

² Zeitsch. anorg. Chem., 33, 251 (1903).

³ Ber., 36, 1565 (1903).

Other elements also yield salts which can be considered as compounds intermediate between halogeno and hydroxo salts, thus, antimony yields the salt 1

$$\left(\mathrm{Sb}_{\mathrm{OH}}^{\mathbf{Fl_{5}}}\right)\!\mathrm{Cs}$$

In the next section large groups of such compounds will be discussed.

Not only dissociating halides, but also other non-dissociating metallic salts ought to give rise to acids through the addition of water. Satisfactory work in this direction has yet to be done.

Such simple behaviour as has been discussed above is only to be observed on hydrating compounds in which the acid residues are so firmly linked to the central atom that they remain undissociated in aqueous solution, for it is only under such conditions that addition can take place without being accompanied by secondary reactions.

The behaviour of electrolytically dissociated halides is much more complicated. Let us suppose that the dissociation is incomplete. Then that portion of the hydrate of a salt which is not split up into metallic and halogen ions will behave as an acid, and the other part will split up into metallic and halogen ions, and hence with such a halide there would be present in aqueous solution both hydrion and chloridion. An example of this type of halide is copper chloride, and its behaviour in solution can therefore be formulated as follows:

$$\begin{array}{c|c} Cl & OH_2 & Cl & O\overline{H} & H^+ \\ Cl & OH_2 & \\ Cl & OH_2 & \\ Cl & O\overline{H} & \\ Cl & O\overline{H} & \\ Cl & \\ Cl & OH & \\ Cl &$$

3. On the Addition Compounds of Metallic Hydroxides which correspond to the Hydrates.

In the aqueous solution of copper chloride beyond hydrion and chloridion there also exists the following ions:

Wells and Metzger, Amer. J. Sci., (4) 11, 451 (1901).

Should these ions have the capacity to form an insoluble compound by combining with one another, then a precipitate will be produced. In the special case of copper chloride this is possible and the basic precipitate so often observed separates:

$$\frac{\text{Cl}_{\text{Cl}}\text{Cu}}{\text{OH}} + + \text{Cu}_{\text{OH}_{2}}^{\text{OH}_{2}} \rightarrow \frac{\text{Cl}_{\text{Cl}}\text{Cu}}{\text{Cl}} < \frac{\text{OH}_{2}}{\text{OH}} > \text{Cu} < \frac{\text{OH}_{2}}{\text{OH}_{2}}$$
Basic salt
$$\rightarrow \left[\text{Cu}_{(\text{OH}_{2})_{2}}^{\text{Cl}}\right] \text{Cu} + 2\text{H}_{2}\text{O}$$

The behaviour of the fluoride very prettily illustrates the F OH_2 formation of this basic salt. The dihydrate Cu dissolves F OH_2 in cold water, but on warming the solution the basic salt:

$$\mathbf{F} : \mathbf{Cu} : \mathbf{HO} : \mathbf{Cu}(\mathbf{OH_2})_2$$

is immediately precipitated.

Basic salts are therefore the salts of the acid resulting from the hydration of halides, and they may be considered also as mixed salts intermediate between halogeno and hydroxo salts. They may be produced either by the addition of metallic hydroxides to neutral salts or vice versâ.

Basic salts formed by the addition of metallic hydroxides to neutral salts are very often difficultly soluble. This property as well as their great stability—the result of being ring compounds—renders their preparation an easy matter. In fact, the formation of such basic salts is a characteristic of some elements. Lead is an example of this kind of element.

For lead yields basic compounds of the general formula:

as a nitrate, chloride, o-, m-, and p-nitrophenate, 2, 4-dinitrophenate, 2, 6-dinitrophenate, pikrate, 2, 3, 4, 6-tetrabrombenzene sulphonate, nitrobenzene- 3, 5-disulphonate, benzyl sulphonate, p-chlorbenzyl sulphonate, nitrobenzyl sulphonate, 2, 4, 6-trinitroresorcinate, etc. Many other divalent metals also yield such basic salts.

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4. On Addition Compounds with Organic Radicles which correspond to the Hydrates.

The organic derivatives of water (alcohol, ether, etc.) combine with salts in the same way as water. The products of such a reaction can be compared to those formed by the addition of alcohol and ether to oxides, for the reactions by which alkyl sulphuric acid and the esters of sulphuric acid are produced:

correspond to the production of the following compounds:

All these compounds, therefore, should be considered as esters of halogenhydroxo acids. After the discovery of oxonium salts a great many compounds of this description were prepared, and following Baeyer's example they were often formulated as oxonium salts.

The supposition that in these compounds we are dealing with tetravalent oxygen is impossible according to my theory. will be made clearer when discussing the oxonium theory. Before leaving this part of the subject, it may be pointed out, that it is possible for organic sulphur and selenium derivatives to form addition compounds in a manner exactly analogous to organic oxygen compounds, e.g.

(n) Conclusions to be deduced from the Consideration of the Addition Compounds.

In the foregoing sections it has been shown that the formation of compounds of the higher order from halides, oxides, sulphides, selenides, cyanides, thiocyanides, nitrates, sulphates, nitrites, sulphites, etc., follow exactly the same laws, and that the organic derivatives of water, sulphuretted hydrogen, etc., may likewise take part in the formation of compounds of the higher order.

But the consideration of the latter compounds led us into the province of molecular compounds. We therefore are compelled to conclude that in principle there is no difference between oxygen salts, halogeno salts, and molecular compounds. The properties of the individual compounds may be widely different, but from the similarity in their method of formation and constitution it must be deduced that they are all compounds of the higher order.

2. The Substitution Compounds.

(a) Substitution Hydrates.

1. Normal Hydrates.

Many metallic salts form hydrates with six molecules of water, as may be seen from the following examples:

 $\begin{array}{llll} & [\operatorname{Ni}(\operatorname{OH}_2)_6]\operatorname{Cl}_2, \ [\operatorname{Ni}(\operatorname{OH}_2)_6]\operatorname{I}_2, \ [\operatorname{Ni}(\operatorname{OH}_2)_6](\operatorname{NO}_3)_2, \ [\operatorname{Ni}(\operatorname{OH}_2)_6](\operatorname{ClO}_3)_2, \\ & [\operatorname{Co}(\operatorname{OH}_2)_6]\operatorname{Cl}_2, \ [\operatorname{Co}(\operatorname{OH}_2)_6](\operatorname{ClO}_3)_2, \ [\operatorname{Co}(\operatorname{OH}_2)_6](\operatorname{BrO}_3)_2, \ [\operatorname{Co}(\operatorname{OH}_2)_6]\operatorname{SpO}_3, \\ & [\operatorname{Zn}(\operatorname{OH}_2)_6](\operatorname{NO}_3)_2, & [\operatorname{Zn}(\operatorname{OH}_2)_6](\operatorname{ClO}_3)_2, & [\operatorname{Zn}(\operatorname{OH}_2)_6](\operatorname{BrO}_3)_2, \\ & [\operatorname{Mg}(\operatorname{OH}_2)_6]\operatorname{Cl}_2, & [\operatorname{Mg}(\operatorname{OH}_2)_6]\operatorname{Br}_2, & [\operatorname{Mg}(\operatorname{OH}_2)_6](\operatorname{BrO}_3)_2, \\ & [\operatorname{Mg}(\operatorname{OH}_2)_6](\operatorname{ClO}_3)_2, \ [\operatorname{Ca}(\operatorname{OH}_2)_6]\operatorname{Cl}_2, \ [\operatorname{Ca}(\operatorname{OH}_2)_6](\operatorname{IO}_3)_2, \ [\operatorname{Sr}(\operatorname{OH}_2)_6]\operatorname{Cl}_2, \\ & [\operatorname{Sr}(\operatorname{OH}_2)_6]\operatorname{Br}_2, & [\operatorname{Fe}(\operatorname{OH}_2)_6]\operatorname{Cl}_3, & [\operatorname{Al}(\operatorname{OH}_2)_6]\operatorname{Cl}_3, & [\operatorname{Al}(\operatorname{OH}_2)_6]\operatorname{Br}_3, \\ & [\operatorname{Al}(\operatorname{OH}_2)_6]\operatorname{I}_3. & \\ & [\operatorname{Al}(\operatorname{OH}_2)_6]\operatorname{I}_3. & \end{array}$

It is noteworthy that many of these hydrates contain the maximum number of water molecules known for the salt in question; and further, all the acid residues have ionogene properties. It is probable, therefore, that their constitutions are similar to those of the hexammine metallic salts; the latter will be discussed later. This supposition finds considerable support in the fact that compounds can be prepared which contain both water and ammonia, and have properties which show them to be compounds intermediate between the hydrates and the metal ammonium compounds.

We assume, consequently, that in the hexahydrates we have salt-like compounds, in which the positive radicle consists of a complex containing the metal and six molecules of water.

The six molecules of water are linked, according to our theory, directly to the central metallic atom, and the acid residues are in

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the second sphere. If this conception of the constitution of the hexahydrates is correct, then it is to be expected that the acid residues, in hydrates which contain less water, will be linked with non-ionogene linkings. The experimental confirmation of this deduction is very difficult, since most of the lower hydrates on solution pass very rapidly into those richer in water. Hence the behaviour of the lower hydrates only very rarely can be examined, but in a few instances it has been found possible to prove the truth of our theory.

In the blue hexahydrate of chromium chloride, $CrCl_3 + 6H_2O$, all the chlorine atoms have ionogene properties, and this hydrate is correctly represented by the formula $[Cr(H_2O)_6]Cl_3$. On losing two molecules of water it is transformed in a green hydrate, $CrCl_3 + 4H_2O$, which on solution only slowly passes into the blue hydrate. It is possible, therefore, in this case to show that in the change from blue to green hydrate two chlorine atoms lose their ionogene character.

Bjerrum was able to prepare a chloropentaquochromchloride in which one chlorine atom had no ionic character. Weinland and Schumann also have been able to prepare chloropentaquochromium sulphate and sulphonate in which the chlorine atoms are unable to act as ions. In the different hydrates of chromium bromide different numbers of bromine atoms are ionizable, thus in the blue hydrate all three appear as ions, while in the green hydrate only one has this property. Finally, Weinland has described and prepared a sulphatopentaquochromiumchloride, $\left[\operatorname{Cr}_{(\mathrm{OH}_2)_5}^{\mathrm{SO}_4} \right]$ Cl, in which the presence of sulphuric acid could not be detected by analytical reactions.

From these examples it is evident that in the chromium salts, at any rate, it is now possible to show a connection between the so-called water of crystallization and the acid residue, and it is natural to expect that this will also be possible when the hydrates of other metals are examined.

¹ Mémoires de l'Ac. Royale des. Sc. et des Lettres de Danemark, 4, 1 (1907).

² Ber., 40, 3091 (1907).

³ Chem. Zeit., 32, 259 (1908).

2. Hydrates containing Double Molecules of Water.

Co-ordination formulæ offer a satisfactory explanation for the constitutions of all known metal ammonium compounds. On the other hand, a great many hydrates exist for which the ordinary co-ordination formulæ offer no satisfactory explanation, because they contain considerably more water than is to be expected from the theory. Thus, it is found that those hydrates which are richest in water, contain not six but twelve molecules, e.g. the alums: $Me^{III}(SO_4)_2R^I + 12H_2O$. Since potassium and ammonium salts are seldom hydrated (and when they are they contain at the maximum one or two molecules of water to a potassium atom or ammonium radicle), it follows that in the alums the presence of twice six molecules of water presents a new type of hydrate. This supposition is supported by the fact that other hydrates are known in which the amount of water present is twice that in the simple hydrates. This is true of the following hydrates:

$$\begin{split} &[Mg(OH_2)_{12}]PtCl_6,^1 \quad [Mn(OH_2)_{12}]PtCl_6,^1 \quad [Ca(OH_2)_{12}]PtBr_6,^1 \\ &[Mg(OH_2)_{12}]PtBr_6,^1 \quad [MnOH_2)_{12}]PtBr_6,^1 \quad [Co(OH_2)_{12}]PtBr_6,\\ &[Zn(OH_2)_{12}]PtBr_6,^1 \quad [Ca(OH_2)_{12}]PtI_6,^1 \quad [Mg(OH_2)_{12}](AuCl_4)_2,^2 \\ &[Zn(OH_2)_{12}](AuCl_4)_2,^2 \quad [Mn(OH_2)_{12}](AuCl_4)_2.^2 \end{split}$$

Now when we recall the fact, that in the liquid state water molecules are associated in pairs it seems quite a probable thing to suppose that they are also associated in these hydrates. Accordingly these abnormal hydrates owe their existence to the addition of polymerized molecules of water to the central metallic atom, and their constitutions may be represented as follows:

This supposition renders it possible to ascribe co-ordination formulæ to even those hydrates which are richest in water. We have, however, no means of deciding how a lower hydrate is derived from hydrates containing six or four double molecules of water. It may be that the double molecules, as such, leaves the complex, or

¹ Dammer, Handb. anorg. Chem., III., 799.

² Bonsdorff, Pogg. Ann., 17, 261 (1829); 33, 64 (1834).

that the double molecule breaks down into the simpler, and in this way reduces the percentage of water present. But these are questions for the future to decide, for the present it is impossible to systematize these hydrates.

3. Hydrates containing Water bound to both Radicles.

The chemistry of the hydrates is further complicated by other phenomena. For hydrates exist in which it is very probable that only part of the water is in combination with the metallic atom, the other part being bound to the acid residue. This appears to be the case in the sulphates, for they crystallize differently to the other salts of the metal in question, i.e. they crystallize with seven instead of six molecules of water. Since it is difficult to see why the metallic atom in the sulphates should combine with seven molecules of water and not six, as in the salts, it seems probable that the seventh molecule is in combination with the sulphate residue. Support is given to this idea by the fact that the introduction into the sulphate molecule of a metallic atom or radicle which themselves yield anhydrous sulphates, so changes the functions of the sulphate radicle that it can no longer take up the seventh molecule of water. Thus, both potassium and ammonium yield anhydrous sulphates; now if either of these radicles are introduced into a sulphate containing seven molecules of water the resulting salt crystallizes with only six water molecules, and we obtain the series $Me(SO_4R_2)_2 + 6H_2O$.

Other phenomena also point to the conclusion that the seventh molecule is differently bound to the remaining six. Thus, the value for the aqueous tension of the water of crystallization in the sulphates of magnesium, nickel, and cobalt show that the seventh molecule is weaker bound than the others. Finally, it can be shown that in other salts, which crystallize with seven molecules of water, the seventh molecule belongs to the acid radicle.

Just the same difference as that observed between sulphates and other salts of divalent metals:

 $CoCl_2 + 6H_2O$, $ZnCl_2 + 6H_2O$, $NiCl_2 + 6H_2O$, $MnCl_2 + 6H_2O$, $CoSO_4 + 7H_2O$, $ZnSO_4 + 7H_2O$, $NiSO_4 + 7H_2O$, $MnSO_4 + 7H_2O$, is to be seen in the following salts:

1. Salts containing six molecules of water:

$$\begin{split} Zn(SiF_6) + 6H_2O,^1 & Zn(SnF_6) + 6H_2O,^2 & Zn(SnCl_6) + 6H_2O,^3 \\ Zn(TiF_6) + 6H_2O,^4 & Zn(ZrF_6) + 6H_2O,^5 & Zn\Big(Nb_{F_5}^O\Big) + 6H_2O,^6 \\ Zn\Big(Mo_{F_5}^O\Big) + 6H_2O,^7 & Zn\Big(Mo_{F_4}^{O_2}\Big) + 6H_2O,^8 & Cd(SnF_6) + 6H_2O,^9 \\ Mg(SiF_6) + 6H_2O,^{10} & Mg(SnF_6) + 6H_2O,^{11} & Mg(SnCl_6) + 6H_2O,^{12} \\ Mg(SiF_6) + 6H_2O,^{13} & Mn(SiF_6) + 6H_2O,^{14} & Mn(SnF_6) + 6H_2O,^{15} \\ Mn(SnCl_6) + 6H_2O,^{16} & Mn(TiF_6) + 6H_2O,^{17} & Co(SiF_6) + 6H_2O,^{18} \\ Co(SnCl_6) + 6H_2O,^{19} & Co\Big(Mo_{F_4}^{O_2}\Big) + 6H_2O,^{20} & Ni(SiF_4) + 6H_2O,^{21} \\ Mi(SnF_6) + 6H_2O,^{22} & Ni(SnCl_6) + 6H_2O,^{23} & Ni(ZrF_6) + 6H_2O,^{24} \\ Ni\Big(Mo_{F_4}^{O_2}\Big) + 6H_2O.^{25} \end{split}$$

- ¹ Marignac, Ann. Min., (5) 15, 256; Jahresber., 1859, p. 108.
- ² Marignac, Ann. Chim. Phys., (3) 60, 257; Jahresber., 1860, p. 139.
- 3 Marignac, ibid.
- ⁴ Marignac, ibid., (3) 60, 304; Jahresber., 1860, p. 98.
- ⁵ Marignac, ibid., (3) 60, 257; Jahresber., 1860, p. 139.
- ⁶ Marignac, ibid., (4) 8, 41 (1866).
- ⁷ Fr. Mauro, Zeitsch. anorg. Chem., 2, 25 (1892).
- ⁸ Delafontaine, Arch. Sci. phys. nat., 30, 240 (1855).
- ⁹ Marignac, Ann. des. Min., (5) 15, 256 (1859).
- 10 Marignac, ibid.
- ¹¹ Marignac, ibid.; Jahresber., 1859, p. 112.
- ¹² Jörgensen, Danske Vid. Selsk. Skr., (5) 6 (1865); Lewy, Ann. Chim. Phys., (3) 16, 308 (1846).
- ¹³ Marignac, Ann. Chim. Phys., (3) 60, 288 (1860); Topsoë and Christiansen, Danske Vid. Selsk. Skr., (5) 9, 648.
 - 14 Marignac, Ann. des. Min., (5) 15, 221 (1859).
 - 15 Jörgensen, loc. cit.
 - 16 Dammer, 2, 593.
- 17 Grailich, Krystall. opt. Untersuch., 75 (1858); Topsoë and Christiansen, Danske Vid. Selsk. Skr., (5) 9, 648; Ann. Chim. Phys., (5) 1, 25 (1874).
 - ¹⁸ Jörgensen, Danske Vid. Selsk. Skr., (3) 6 (1865).
- Delafontaine, Arch. Sc. phys. nat., 30, 240 (1855).
 Berzelius, Pogg. Ann., 1, 198 (1824); Marignac, Ann. des. Min., (5) 15, 262 (1859).
 - 21 Marignac, Jahresber., 1859, p. 112.
 - 22 Jörgensen, Danske Vid. Selsk. Skr., (5) 6.
 - ²³ Marignac, Jahresber., 1860, p. 137; Annalen, 116, 359 (1860).
 - ²⁴ Delafontaine, Arch. Sci. phys. nat., 30, 1240 (1855).
 - ²⁵ Petersen, J. pr. Chem., (2) 40, 52 (1889).

2. Salts containing seven molecules of water:

$$\begin{split} & \text{Co}(\text{Cr}\mathbf{F}_5) + 7\text{H}_2\text{O},^1 & \text{Co}(\text{V}\mathbf{F}_5) + 7\text{H}_2\text{O},^2 & \text{Co}(\text{V}^{\text{O}}_{\mathbf{F}_4}) + 7\text{H}_2\text{O},^3 \\ & \text{Ni}(\text{Cr}\mathbf{F}_5) + 7\text{H}_2\text{O},^4 & \text{Ni}(\text{V}\mathbf{F}_5) + 7\text{H}_2\text{O},^5 & \text{Ni}(\text{V}^{\text{O}}_{\mathbf{F}_4}) + 7\text{H}_2\text{O},^6 \\ & \text{Zn}(\text{V}\mathbf{F}_5) + 7\text{H}_2\text{O},^7 & \text{Zn}(\text{V}^{\text{O}}_{\mathbf{F}_3}) + 7\text{H}_2\text{O},^8 & \text{Zn}(\text{V}^{\text{O}}_{\mathbf{F}_4}) + 7\text{H}_2\text{O},^9 \\ & \text{Cd}(\text{V}\mathbf{F}_5) + 7\text{H}_2\text{O},^{10} & \text{Cd}(\text{V}^{\text{O}}_{\mathbf{F}_4}) + 7\text{H}_2\text{O}.^{11} \end{split}$$

¹ Dammer, 3, 713.

² Piccini and Giorgio, Atti R. Accad. dei Lincei, Roma, 1890, II. Sem., pp. 130-132.

3 Petersen, loc. cit.

⁴ Dammer, 3, 713.

⁵ Piccini and Giorgio, Atti R. Accad. dei Lincei, Roma, 1890, II. Sem., pp. 130-132.

⁶ Ibid. ¹ Ibid. ⁸ Ibid. ⁹ Ibid. ¹⁰ Ibid. ¹¹ Ibid.

Since the constitution of the acid radicle of the potassium and ammonium salts containing one molecule of water corresponds to those containing seven:

$$\left[V_{OH_{2}}^{F_{5}} \right] \! (NH_{4})_{\!_{2}}^{\ _{1}} \quad \left[Cr_{OH_{2}}^{F_{5}} \right] \! K_{2}^{\ _{2}} \quad \left[V_{OH_{2}}^{O} \right] \! (NH_{4})_{\!_{2}}^{\ _{3}}$$

¹ Christensen, J. pr. Chem., (2) 35, 161 (1887).

² Piccini and Giorgio, Atti R. Accad. dei Lincei, Roma, 1890, II. Sem., p. 130.

³ Baker, Ber., 11, 1722 (1848).

it follows that the acid radicle is co-ordinatively saturated, and the complete constitutional formulæ for compounds containing seven molecules of water of crystallization described in the above list are to be written:

$$\begin{split} & \big[\text{Co}(\text{OH}_2)_6 \big] \Big[\text{Cr}_{F_5}^{\text{OH}_2} \big] \quad \big[\text{Co}(\text{OH}_2)_6 \big] \Big[\text{V}_{F_5}^{\text{OH}_2} \big] \quad \big[\text{Co}(\text{OH}_2)_6 \big] \Big[\text{V}_{F_4}^{\text{OH}_2} \big] \\ & \big[\text{Ni}(\text{OH}_2)_6 \big] \Big[\text{Cr}_{F_5}^{\text{OH}_2} \big] \quad \big[\text{Ni}(\text{OH}_2)_6 \big] \Big[\text{V}_{F_5}^{\text{OH}_2} \big] \quad \big[\text{Ni}(\text{OH}_2)_6 \big] \Big[\text{V}_{F_4}^{\text{OH}_2} \big] \\ & \big[\text{Zn}(\text{OH}_2)_6 \big] \Big[\text{V}_{F_5}^{\text{OH}_2} \big] \quad \big[\text{Zn}(\text{OH}_2)_6 \big] \Big[\text{V}_{F_4}^{\text{OH}_2} \big] \quad \big[\text{Zn}(\text{OH}_2)_6 \big] \Big[\text{V}_{F_4}^{\text{OH}_2} \big] \\ & \big[\text{Cd}(\text{OH}_2)_6 \big] \Big[\text{V}_{F_5}^{\text{OH}_2} \big] \quad \big[\text{Cd}(\text{OH}_2)_6 \big] \Big[\text{V}_{F_4}^{\text{OH}_2} \big] \end{split}$$

These formulæ are in satisfactory agreement with the suggested division of the seven water molecules in the sulphates.1

From these considerations the conclusion is to be drawn that when ascribing the constitution to the hydrates the water molecules

must be divided between both basic and acidic components.

Before concluding this section, attention may be drawn to the fact that starting from quite a different standpoint Kurnakow² came to the conclusion expressed above. Since the hydration of certain elements—e.g. copper, cobalt, nickel—is accompanied by a change of colour, it is possible in many cases to decide whether the water has been taken up by the acid residue or not. Thus, it is inferred from the reddish-brown colour of lithium copper chloride, CuCl₂ + LiCl + 3H₂O, that all the water is linked to the lithium, whereas in potassium copper chloride, CuCl₂ + KCl + 2H₂O, which is blue, the water must be bound to the copper.

(b) Substitution Compounds formed by Organic Oxygen Compounds.

We have already seen that not only water, but also organic oxides are able to take part in the formation of addition compounds, and it therefore appears probable that they will also be able to take part in the formation of substitution compounds.

The work of Mentschutkin confirms this assumption, for he prepared from the most varied organic oxides the following compounds:

(a) Compounds with alcohol:

 $[\mathrm{Mg}(\mathrm{CH_3}\cdot\mathrm{OH})_6]\mathrm{Cl}_2,\ [\mathrm{Mg}(\mathrm{C_2H_5OH})_6]\mathrm{Cl}_2,\ [\mathrm{Mg}(\mathrm{C_2H_5}\cdot\mathrm{OH})_6](\mathrm{NO_3})_2$

(b) With acids:1

[Mg(H·COOH)₆]Br₂, [Mg(CH₃COOH)₆]Br₂,

 $[Mg(CH_3 \cdot COOH)_6]I_2, [Mg(C_2H_5COOH)_6]I_2, [Mg(C_3H_7 \cdot COOH)I_2, [Mg[(CH_3)_2CHCOOH]_6]I_2.$

(c) With esters : 2

$$\begin{split} & [Mg(C_2H_3O_2CH_3)_6]I_2, \quad [Mg(C_2H_3O_2C_2H_5)_6]I_2, \quad [Mg(C_2H_3O_2C_3H_7)_6]I_2, \\ & [Mg(C_2H_3O_2C_4H_9(iso)_6]I_2, \quad [Mg(C_2H_3O_2C_5H_{11}(iso)_6]I_2. \end{split}$$

- 1 Chem. Zeit., 30, 129 (1906); Zeitsch. anorg. Chem., 54, 87 (1907).
- ² Chem. Zeit., 29, 788 (1905).

[Me(OH₂)₆] · SO₄H

The following constitutional formula appears to me to be the most probable one for these sulphates:

² Zeitsch. anorg. Chem., 17, 205 (1898).

- (d) With ketones: 1 [Mg(CH₃COCH₃)₆]I₂.
- (e) With urea: [Ca(OCN₂H₄)₆](NO₃)₂.

¹ Iswestija d. Petersb. polyt. Inst., 6, 39 (1906).

To this list are to be added the compounds discovered by Sell ¹ and which were examined later by Kalkmann and me, ² *i.e.* the chromium salts of urea:

$$[\operatorname{Cr}(\operatorname{OCN_2H_4})_6]X_3$$

It should be noted that there are many compounds described in the literature which contain four organic molecules in the complex. However, at present it is impossible to decide whether these complexes are addition or substitution compounds, and hence they are omitted from the present discussion.

It is important, however, to notice that in spite of having taken extraordinary care and trouble Mentschutkin was unable to prepare a complex which contained more than six molecules of an organic oxide, and this is all the more important when it is remembered that the behaviour of hydrates is much more complicated.

(c) Substitution Compounds containing Metallic Hydroxides.

When discussing addition compounds the hydroxo salts were considered, and it was seen that they were formed with particular ease from such compounds as Me OH, and neutral salts according to the equation:

$$\mathbf{X} \cdot \mathbf{HO} \cdot \mathbf{HO} \cdot \mathbf{Me} = \mathbf{X} \cdot \mathbf{HO} \cdot \mathbf{Me} \times \mathbf{HO} \cdot \mathbf{Me}$$

Since in these addition compounds one molecule of the dihydraxide plays the same $r\hat{o}le$ as two molecules of water in the hydrates, so is it to be expected that complex compounds having the general formula $\left[\mathrm{Me}\begin{pmatrix}\mathrm{HO}\\\mathrm{HO}\mathrm{Me}\end{pmatrix}_3\right]\mathrm{X}_2$ could be prepared from the hexahydrates $\left[\mathrm{Me}(\mathrm{OH}_2)_6\right]\mathrm{X}_2$ were complete substitution of the water molecules possible. An examination of the basic metallic salts revealed the

¹ Jahresber., 1882, p. 382. ² Annalen, 322, 302 (1902).

fact that such a group does exist, and it is proposed to call them "hexol salts." Since I have already made a list of these compounds, it is unnecessary to discuss them here.

(d) Substitution Compounds formed with Substituted Hydroxo Salts.

The formula of the hexol salts:

$$\left[\mathrm{Me}\left(\frac{\mathrm{HO}}{\mathrm{HO}}\mathrm{Me}\right)_{_{3}}\right]\mathrm{X}_{_{2}}$$

leads us to expect that the hydrogen of the hydroxyl groups can be replaced by other radicles; in this way compounds with the following general formula are obtained:

$$\left[\mathrm{Me}\left(\frac{\mathrm{RO}}{\mathrm{RO}}\mathrm{Me}\right)_{_{3}}\right]\mathrm{X}_{_{2}}$$

where R is the substituting radicle. When R becomes an acid radicle, we obtain the formula of a peculiar type of complex salts in which the three salt molecules Me $\stackrel{\cdot}{OR}$ assume the functions of the dihydroxides in the hexol salts. Such complex salts exist in great numbers, and some of the classes play a very important $r \delta l e$ in mineral chemistry. I should like, in order to point out the importance of this type of complex salt, to draw attention to two groups, the first of which is purely of chemical interest, and the second derives its importance from the standpoint of mineral chemistry. The groups referred to are the groups of Schweinfurt greens and the Apatite group. In the former compounds R = AsO, and in the latter $R = PO_3Me$, AsO_3Me or VO_3Me , and they consequently have the formulæ:

$$\begin{bmatrix} Me \begin{pmatrix} OAsO \\ > Me \\ OAsO \end{pmatrix}_3 \end{bmatrix} X_2 \quad and \quad \begin{bmatrix} Me \begin{pmatrix} ORO_3Me \\ > Me \\ ORO_3Me \end{pmatrix}_3 \end{bmatrix} X_2$$

The number of these compounds is very large, as may be seen by referring to my communication.2

¹ Ber., 40, 4442 (1907).

² Ibid., p. 4447.

3. Compounds of Higher Order containing Nitrides, Phosphides, etc.

1. Addition Compounds.

(a) Double Nitrides.

Up to the present only a few nitrides are known in the pure condition, e.g. magnesium nitride, those of the alkaline metals and alkaline earths, etc. Still fewer double nitrides are known. Some amido- and imido-compounds of the elements can be considered as double nitrides. Such compounds have undergone thorough examination in the last few years. The following may be cited as examples:

$$B(NH_2)_{3}$$
, $B_2(NH)_{3}$, $As(NH_2)_{3}$, $P(NH_2)_{4}$, $Si(NH_2)_{4}$, $Si(NH_2)_{4}$, SiN_2H_2 , P_2NH_2 , $Ba(NH_2)_2$, $NaNH_2$, $LiNH_2$.

- ¹ Joannis, Compt. rend., 135, 1106 (1902).
- ² Joannis, ibid., 139, 364 (1904).
- 3 Hugot, ibid., 139, 54 (1904).
- ⁴ Joannis, ibid., 139, 364 (1904).
- ⁵ Vigouroux and Hugot, loc. cit., 136, 1670 (1903).
- ⁶ Stock, Ber., 36, 1120 (1903).
- ⁷ Mentzel, Compt. rend., 135, 740 (1902).

In the group of nitrido salts derived from hydrazoic acid, one is known; it is formed by the union of thalli- and thallanitride:

$$\begin{bmatrix}
\mathbf{N}_{3} \\
\mathbf{N}_{3}
\end{bmatrix} \mathbf{T}\mathbf{l} + \mathbf{N}_{3}\mathbf{T}\mathbf{l} = \begin{bmatrix}
\mathbf{N}_{3} \\
\mathbf{N}_{3}
\end{bmatrix} \mathbf{T}\mathbf{l} - \mathbf{N}_{3}$$

$$\mathbf{T}\mathbf{l} = \begin{bmatrix}
\mathbf{N}_{3} \\
\mathbf{N}_{3}
\end{bmatrix} \mathbf{T}\mathbf{l} - \mathbf{N}_{3}$$

⁸ Dennis, Doan and Gill, J. Amer. Soc., 18, 970 (1896).

An interesting group of complex salts, which possibly may be considered as nitrido salts, may be prepared from imido acids.

L. Tschugaeff¹ has shown in the case of copper and nickel succinimide, and H. Ley and F. Werner² in the case of the copper salt of camphoracidimide and copper phthalimide, that these salts are able to combine with two molecules of alkalimide to form complex salts of the following general formula:

$$[MeIm_4]R_2$$

1 Ber., 40, 1978 (1907).

² 1bid., p. 706.

The following complex salts of this class have been described:

[CuSu₄]K₂ + 6H₂O, light reddish-violet; [CuSu₄]Na₂ + 5H₂O, blue; [CuSu₄]Rb₂ + 2 ₂O, reddish-violet; [CuSu₄]Li + H₂O,

ultramarine-blue;

[CuSu₄]Cs + 2H₂O, red-violet;

 $[CuCph_4]K_2$, red-violet; $[Cu(Pht)_4]K_2 + 4H_2O$, red-violet.

Tschugaeff and also Ley have pointed out that the akalibiuretcopper compounds, which cause the biuret reaction, also belong to this class of compounds.

Double cyanides, the cyanide residue of which is linked to the central nitrogen atom, are also to be formulated as double nitrides. It appears, however, from the work of Hofmann and Bugge¹ on the behaviour of nitriles and carbilamines that in most double cyanides the cyanide residue is bound to the central metal atom by carbon. In agreement therewith it has been found that carbylamines result from the action of alkylhalides on the silver and lead cyanides.

Franklin and Fitzgerald ² have prepared lately a group of salts—the amido salts—which bear to the nitrido salts the same relationship as the hydroxo salts do to the oxo salts. Only two members of this group are known at present, *i.e.* tetraamidozincoate and hexamidostanneate of potassium:

$$\begin{bmatrix} \mathbf{H_2N} & . & . & \mathbf{NH_2} \\ & \mathbf{Zn} & \\ \mathbf{H_2N} & . & . & \mathbf{NH_2} \end{bmatrix} \mathbf{K_2} \quad \text{and} \quad \begin{bmatrix} \mathbf{H_2N} & . & . & \mathbf{NH_2} \\ \mathbf{H_2N} & . & . & \mathbf{NH_2} \\ \mathbf{H_2N} & . & . & . & \mathbf{NH_2} \end{bmatrix} \mathbf{K_2}$$

The latter compound brings out very clearly the complete analogy between it and the corresponding hydroxyl compound of tin:

$$[\operatorname{Sn}(\operatorname{OH})_6]K_2, [\operatorname{Sn}(\operatorname{NH}_2)_6]K_2$$

On heating the amido salts change into imido and nitrilo salts, but as yet their properties have not received a thorough examination.

(b) Compounds formed by the Addition of Ammonia to Oxides and Sulphides.

Ammonia, acting as a nitride, can take part in the formation of compounds of the higher order in the same way as halides and oxides. It combines, therefore, with oxides, sulphides, etc.

¹ Ber., 40, 1772 (1907).

² J. Amer. Soc., 29, 657, 1274, 1693 (1907).

The analogy existing between such addition products of ammonia and those compounds which we have dealt with already is made clear through the following formulæ:

Although there can be no doubt that the nitrogen of the ammonia is bound directly to the central atom of the oxide molecule in the compounds resulting from the addition of ammonia to oxides, yet the process by which this addition is brought about is very uncertain, because the constitution of the final products give us no information. To be sure, it appears as if the step was one of addition, the resulting product then being transformed into a valency compound:

but it is impossible to prove this assumption.

This difficulty is not removed by the fact that tertiary amines, in which such a transformation is impossible, form addition-products in a similar way:

because it is possible to give such compounds a valency formula by supposing that nitrogen becomes pentavalent:

$$\begin{array}{ccc}
O & CH_3 & \rightarrow & O & O \\
OS & N & CH_3 & \rightarrow & O & N(CH_3)_3
\end{array}$$

On the other hand, when the phenomena connected with formation of ammino-compounds (discussed in the next section) are considered, it will be hardly possible to doubt that the first stage in the formation of acid amides consists in the mutual saturation of the auxiliary valencies of nitrogen and the central atom of the oxide.

The compounds produced by the action of ammonia on oxides can be considered as mixed salts resulting from the action of the

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oxygen acids upon the as yet unknown nitrido acids. The numbers of representatives of this group are small. Amongst the halogen acids such compounds are quite unknown, and in the oxygen group only two well-defined examples are known:

In the nitrogen-group the first member forms the compound O_2N . NH_2 , and phosphorus provides us with an immense number of compounds resembling acid amides. The work of Gladstone and Holmes 1 and also that of Stock 2 has made us well acquainted with the latter compounds. Stokes 3 has prepared a series of polymeric compounds called the polymetaphosphine acids, $NP(OH)_2$.

Derivatives of carbonic and thiocarbonic acid which resemble amides are also known. Well-defined compounds are given by the union of ammonia and amines with chromium tetroxide, e.g.

$$O_2$$

 $OCr(NH_3)_3$, $OCr en + 2H_2O$, $OCr \cdot C_6H_{12}N_4^4$
 O

while Rosenheim and Jacobsen 5 have described and prepared the following compounds:

Lastly, osmium gives us osmiam acid, the constitution of which Dinklage 6 and I have shown to be represented by:

$$\left(\operatorname{Os}_{N}^{\operatorname{O}_{3}}\right)\!\mathbf{H}$$

(c) Ammino Compounds formed by Addition.

Ammonia and amines form addition compounds with the most varied metallic compounds. The simplest compounds of this class are those in which the acid residue is linked to the metal by nonionogene bonds, because in such cases it is possible to show that

¹ Trans., (2) 2, 225 (1864); 3, 135 (1865); 4, 290 (1866); 6, 64, 261 (1868); 7, 15 (1869).

² Ber., 39, 1967 (1906).

³ Zeitsch. anorg. Chem., 19, 38 (1899).

⁴ Hofmann, Ber., 39, 3181 (1906).

⁵ Zeitsch. anorg. Chem., 50, 297 (1906).

⁶ Ber., 34, 2699 (1901).

the addition of ammonia or amines cannot be explained by the doctrine of valency. This is the case in the following addition compounds of platechloride, platochloride, and cobaltinitrite:

$$Cl_4Pt$$
 NH_3
 NH_3

All these compounds in aqueous solution conduct electricity so badly that it is impossible to suppose that the acid residues are present as ions. This conclusion is confirmed by the fact that the presence of chlorine and nitritous acid cannot be proved by analytical reactions. Consequently we must conclude that the entrance of ammonia in the molecule has been without effect upon the linking of the acid residues. The only possible explanation is to assume that the ammonia molecule is linked to the metallic atom by auxiliary valencies. A list of such addition compounds is given below, and it will be seen that the composition of these compounds brings out very clearly the co-ordination number of the metallic atom in question.

$$\begin{split} F_3B \cdot NH_3,^1 & (CH_3)_3B \cdot NH_3,^2 & (H_5C_2)_3B \cdot NH_3,^2 & F_3B \cdot NCCH_3,^3 \\ & Cl_2Sn(NH_3)_2,^4 & I_2Sn(NH_3)_2,^4 & (C_2H_5)_3Sn(NH_3)_2,^4 \\ & (C_2H_6)_2Sn(NH_3)_2,^4 & (C_2H_5)_3Sn(NH_3)_2,^4 \\ & (CH_3)_3Sn(NH_3)_2,^4 & (CH_3)_3Sn \cdot 2C_6H_5NH_2,^4 \\ & (C_2H_6)_3Sn \cdot 2C_6H_5NH_2,^4 & (CH_3)_3Sn \cdot 2C_6H_5NH_2,^4 \\ & (C_2H_6)_3Sn \cdot 2C_5H_{11}NH_2,^4 & \\ & Cl_4SnPy_2,^4 & Br_4SnPy_2,^4 & Cl_2SnPy_2,^4 & (C_2H_5)_2SnPy_2,^4 \\ & (C_2H_6)_2^2SnPy_2,^4 & (C_2H_5)_2^2SnPy_2,^4 & (C_2H_5)_2^2SnPy_2,^5 \\ & Cl_4Sn(NCCH_3)_2,^5 & Cl_4Sn(NCC_2H_5)_2,^5 & Cl_4Sn(NCC_6H_5)_2,^5 \\ & Cl_4Ti(NCCH_3)_2,^5 & Cl_4Ti(NCC_2H_5)_2,^5 & Cl_4Ti(NCC_6H_5)_2,^5 \\ & Cl_5Sb(NCCH_3),^5 & Cl_5Sb(NCC_2H_5),^5 & Cl_5Sl_2(NCC_6H_5),^5 \\ & Cl_4Pt(NCC_2H_8)_2,^5 & Cl_3Au(NCCH_3),^5 & Cl_3Au(NCC_2H_5),^5 \\ & Cl_4Pt(NCC_2H_8)_2,^5 & Cl_4Pt(NCC_2H_8)_2,^5 & Cl_3Au(NCCH_8)_2,^5 \\ & Cl_4Pt(NCC_2H_8)_2,^5 & Cl_4Pt(NCC_2H_8)_2,^5 & Cl_4Pt(NCC_2H_8)_2,^5 \\ & Cl_4Pt(NCC_2H_8)_2,^5 & Cl_4Pt(NCC_2H_8)$$

¹ Davy, Phil. Trans., 1812, p. 368.

² Frankland, Annalen, 124, 129 (1862).

³ Patein, Ber., 24, 734 (1891).

Werner and Pfeiffer, Zeitsch. anorg. Chem., 17, 82 (1898).
Henke, Annalen, 106, 280 (1858).

1 Werner, Zeitsch. anorg. Chem., 15, 164 (1897).

- ² Werner and Bindschedler (Bindschedler, Dissertation, Zürich, 1901).
- 3 Wiede and Hofmann, Zeitsch. anorg. Chem., 11, 379 (1896).

4 Werner and Grun, Ber., 38, 4003 (1905).

⁵ Werner, Ber., 39, 2673 (1906).

6 Cleve, Kong. Vet. Akad. Handl., 10, No. 93, pp. 41, 63 (1871).

7 Pfeiffer, Zeitsch. anorg. Chem., 24, 282 (1900).

8 Hedin, Om pyridinens platinabasers, p. 8 (1887); Jörgensen, J. pr. Chem., 33, 504 (1886).

9 Werner and de Vries, Annalen, 364, 9 (1909).

Cobalt compounds with a-Dioximes.1

(a) Derivatives of dimethylglyoxime:

(b) Derivatives of methylethylglyoxime:

$$\mathbf{H}_{3}\mathbf{N}\mathbf{Co}_{\mathbf{NO}_{2}}^{\mathbf{D}_{2}\mathbf{H}_{2}}, \ \mathbf{Py}\mathbf{Co}_{\mathbf{SCN}}^{\mathbf{D}_{2}\mathbf{H}_{2}}.$$

(c) Derivatives of methylglyoxime:

$$\mathbf{H_{3}NCo_{Cl}^{D_{2}H_{2}}}$$
.

Determinations of electrical conductivity have been made of the following compounds, and it has been shown that they conduct so poorly that it is impossible for them to exist in solution as ions.

- Werner and Miolati, Zeitsch. physikal. Chem., 12, 35 (1893); 14, 506 (1894).
- ² Tschugaeff, Ber., 39, 2692 (1906).

³ Tschuaeff, Ber., 40, 3499 (1907).

4 Werner and de Vries, Annalen, 364, 9 (1909).

¹ Tschugaeff, Ber., 40, 3504 (1907).
² D₂H₂ means 2 mols. gloxime.

(d) Addition Compounds formed with Phosphides, Arsenides, etc.

Phosphine, arsine, etc., form addition compounds analogous to those formed by ammonia and amines.

The following list affords examples of these compounds:1

The addition compounds which are formed by phosphorus trichloride and arsenic trichloride with certain salts of the noble metals are very peculiar. Examples of these are:

$$\text{Cl}_3\text{Ir}(\text{PCl}_3)_3$$
, $\text{Br}_3\text{Ir}(\text{PBr}_3)_3$, $\text{Br}_4\text{Ir}(\text{PCl}_3)_2$, $\text{ClAu} \cdot \text{PCl}_3$, $\text{BrAu} \cdot \text{PBr}_3$, $\text{BrAu} \cdot \text{PCl}_3$.

¹ Schützenberger, Compt. rend., 70, 1287 (1870).

² Schützenberger and Fontaine, Bull. Soc. Chim., (2) 17, 482 (1872); (2) 18, 101, 148 (1872).

³ Schützenberger, Ber., 5, 222, 535 (1872).

4 Fink, Compt. rend., 115, 176 (1892).

⁵ Geisenheimer, Compt. rend., 110, 40, 1004, 1336 (1890); 111, 40 (1890).

6 Geisenheimer, Ann. Chim. Phys., (6) 23, 249 (1891).

⁷ Lindet, Compt. rend., 98, 1382 (1884); 101, 164 (1885).

These compounds are important, because their chemical behaviour opens up their constitution very distinctly. On the one hand, alcohol and water are without action on the chlorine atoms attached to the metal; but on the other hand, it is well known that these reagents replace the chlorine of phosphorus and arsenic by hydroxyl, or alkyloxyl groups. Hence on the solution of these compounds in water or alcohol the following reactions take place:

In the same way, water attacks the compound Cl₂Pt . PCl₃ and . PCl₃

¹ Cahours and Gal, Compt. rend., 70, 849, 1380 (1870); 71, 208 (1870).

yields a hexabasic acid to which the following constitution must be given:

Rosenheim and Löwenstamm 1 have studied platinum compounds of this type. Their work has led them to the conclusion that the phosphortrichlorplato chlorides are completely analogous to the platinum ammonium compounds, and also that the existence of trivalent phosphorus in these compounds must be considered as proved.

To the same class of compounds also belong the copper halides of the esters of phosphorous acid which Arbusow 2 prepared. They have the following constitutional formulæ:

$$XCu \cdot P(OR)_3$$
 and $XCu \cdot \frac{P(OR)_3}{P(OR)_3}$

Since these compounds are produced by the direct addition of the components, it is perhaps not superfluous to draw attention to the analogy which exists between them and the alkylhalide addition compounds prepared by Michaelis and Kaehne³:

$$\begin{array}{c|c}
RO \\
RO \\
RO
\end{array}
P + CuX = RO \\
RO
P + CuX and RO \\
RO
P + CH3I = RO \\
RO
P + CH3)I$$

The only difference which exists between both reactions is that the iodine, in the methyl iodide addition product, has ionogene properties—the result of the occupation of all the co-ordination positions on the carbon atom.

2. Substitution Compounds.

(a) General.

When a compound which is co-ordinatively saturated takes up more ammonia, then for every additional molecule an acid residue passes from a direct into an indirect linking, thereby receiving

ionogene properties. To demonstrate this behaviour let us consider the co-ordinatively saturated compounds $(O_2N)_3Co(NH_3)_3$ and $Cl_4Pt(NH_3)_2$.

When ammonia acts on $(H_3N)_3Co(NO_2)_3$ the following compounds can be obtained:

$$(H_3N)_3Co(NO_2)_3 + NH_3$$
, $(H_3N)_3Co(NO_2)_3 + 2NH_3$, $(H_3N)_3Co(NO_2)_3 + 3NH_3$.

In these compounds each molecule of ammonia as it enters the complex expels a NO₂-group from the first into the second or dissociable zone. The properties of these compounds are represented therefore by the constitutional formulæ:

$$\begin{bmatrix} (H_{3}N)_{3}C_{0} < \begin{matrix} NO_{2} \\ NO_{2} \\ NH_{3} \end{bmatrix} NO_{2} & \begin{bmatrix} (H_{3}N)_{3}C_{0} < \begin{matrix} NO_{2} \\ NH_{3} \\ NO_{2} \\ NH_{3} \end{bmatrix} NO_{2} \\ (H_{3}N)_{3}C_{0} < \begin{matrix} NH_{3} \\ NH_{3} \\ NO_{2} \\ NH_{3} \end{bmatrix} \begin{matrix} NO_{2} \\ NO_{2} \\$$

The characteristic properties of these substitution ammino-complexes not only find expression in their chemical behaviour, but also, as has been mentioned already, in their electrical conductivity.

More than three molecules of ammonia are never taken up, and hence the formation of these complexes is complete when all six co-ordination positions are occupied by ammonia. The co-ordinatively saturated compound $(H_3N)_2PtCl_4$ displays a completely analogous behaviour, for the substitution of ammonia produces the following compounds:

$$(H_3N)_2PtCl_4 + NH_3$$
, $(H_3N)_2PtCl_2 + 2NH_3$, $(H_3N)_2PtCl_2 + 4NH_3$

And since the entrance of ammonia confers ionongene properties upon the chlorine, the following structural formulæ give expression to these differences:

These changes can be followed in the increased electrical conductivity of these compounds. The composition and behaviour of such compounds can be expressed by the following general formulæ:

(a) divalent elements:

$$[Me(NH3)6]X2 [Me(NH3)5]X$$

(b) trivalent elements:

$$\begin{bmatrix} Me(NH_3)_6 \end{bmatrix} X_3 \qquad \begin{bmatrix} Me_{(NH_3)_5}^X \end{bmatrix} X_2 \qquad \begin{bmatrix} Me_{(NH_3)_4}^X \end{bmatrix} X$$

(c) tetravalent elements:

$$[Me(NH_3)_6]X_4 \ [Me_{(NH_3)_5}^{X}]X_3 \ [Me_{(NH_3)_4}^{X_2}]X_2 \ [Me_{(NH_3)_3}^{X_3}]X$$

These type formulæ are of great importance to the systematics of substitution ammino-complexes, and the following nomenclature is proposed for these compounds.

(b) Nomenclature.1

- 1. Names obtained from the colour of the compounds are to be avoided.
- 2. The name of the resulting complex is to be made up by placing side by side the names of the components.
- 3. The names of the atoms (or radicles) which are linked to the central metallic atom are to be placed before the name of this central atom. When carrying this out the following order is to be preserved: The names of the acid residues come first, then follow the names of the groups which resemble ammonia, and directly before the name of the metallic atom are to be placed the number of ammonia molecules.
- 4. The molecule of ammonia is to be expressed by the word ammine (spelt with a double m), in order to distinguish it from the organic amine. Water, after Palmaer's suggestion is expressed by aquo.
- 5. The names of the acid residues which are not in the first binding zone are placed after the name of the central metallic atom.

Examples of these rules are-

$$\begin{split} & [\operatorname{Cr}(NH_3)_6](NO_3)_3, & \operatorname{Hexamminchrominitrate}; \\ & \begin{bmatrix} O_2N_{\text{Cl}}\operatorname{Coen}_2 \end{bmatrix}\operatorname{Br}, & \operatorname{Chloronitritodiethylendiamincobaltibromide}; \\ & [\operatorname{Co}_{(NH_3)_4}^{(OH_2)_2}]\operatorname{Cl}_3, & \operatorname{Diaquotetrammincobaltichloride}; \\ & [(HO)_2\operatorname{Pt}(NH_3)_4]\operatorname{Cl}_2, & \operatorname{Dihydroxotetramminplatechloride}. \end{split}$$

(c) Review of the Ammino Complexes formed by Substitution.

(a) Type [Me(NH₃)₆]X_n, Hexammin salt.

All members of this group contain a complex positive ion, consisting of a central metallic atom, surrounded by six NH_3 -groups. The valency of the complex radicle is the same as that of the central metallic atom, for the NH_3 -groups are attached by auxiliary valencies, thus leaving the principal valencies free. Hexammines are known which contain tetravalent, trivalent, and divalent central metallic atoms. The yellow hexammines of cobalt were the first to be examined and therefore the whole class is sometimes spoken of as the luteo salts.

The number of hexammines which are known already is very large. The type $[Me(NH_3)_6]X_3^{-1}$ has received the most attention. Nevertheless a great many divalent metallic salts are known, as may be seen from the following list:

Dpy means one mol. of a-Dipyridyl and Phn. Phenanthroline.

- ¹ Rose, J. pr. Chem., 7, 266 (1836); 19, 445 (1840).
- ² Uhlenhuth, Annalen, 307, 332 (1899).
- ³ Curtius, J. pr. Chem., (2) 50, 343 (1894).
- ⁴ Blau, Monatsh., 19, 647 (1898).
- ⁵ Werner, Zeitsch. anorg. Chem., 21, 210 (1899).
- 6 Schüler, Annalen, 87, 34 (1853); Wells, Amer. Chem. J., 9, 304 (1887).
- ⁷ Varet, Bull. Soc. Chim., (3) 5, 843 (1891).
- ⁸ Richards, Ber. 23, 3790 (1890).
- Rammolsberg, Annalen, 55, 244 (1845); Frémy, Ann. Chim. Phys., (3) 35, 257 (1852).

¹ See the list in Ber., 40, 20 (1907).

A complete list of hexammine salts has been published by Pfeiffer.1

The compounds of this type are obtained from the former type by the loss of an ammonia molecule:

$$[\operatorname{Cr}(\mathbf{N}\mathbf{H}_3)_6]\operatorname{Cl}_3 = \mathbf{N}\mathbf{H}_3 + \left[\operatorname{Cr}^{\operatorname{Cl}}_{(\mathbf{N}\mathbf{H}_3)_5}\right]\operatorname{Cl}_2$$

They can be obtained also by other means. But for our present object it is only of importance that the complex contains only five NH₃-groups and one acid residue in the non-ionogene condition.

In hexammincobaltichloride $[\operatorname{Co}(\operatorname{NH}_3)_6]\operatorname{Cl}_3$ all three chlorine atoms are present as ions, and are therefore immediately precipitated in the cold by silver nitrate. From this compound the loss of a molecule of ammonia yields chloropurpure ochloride $[\operatorname{Co}(\operatorname{N}_3H_5)]\operatorname{Cl}_2$. In this compound only two chlorine atoms are in the ionic condition, for only two can be precipitated by silver nitrate in the cold; the third chlorine behaves like organic chlorine, e.g. like chlorine in chlorethane.

This difference in the behaviour of the acid residues is very characteristic, and may be shown in most cases very clearly. The following reactions serve to bring out the difference: (a) The acid residues which act as ions react with sodium platinum chloride and potassium platinous chloride, while those which are incapable of acting as ions do not give this reaction, e.g.

$$\left[Co_{(\mathrm{NH_3})_5}^{\mathrm{Cl}}\right]Cl_2 + H_2PtCl_6 = \left[Co_{(\mathrm{NH_3})_5}^{\mathrm{Cl}}\right]PtCl_6 + 2HCl$$

(b) The ionic chlorine is liberated as hydrochloric acid when the compound is treated in the cold with concentrated sulphuric acid, while the non-ionic chlorine remains unacted upon.

Such compounds as $\left[Me_{(NH_3)_5}^X\right]X_n$ are known only with trivalent elements, and since the first compounds of this type studied had a bluish-red colour, the general name of purpureo-salts has been given to this group. According to their composition they should be called the acidopentammines. It may be mentioned that

the acid residue, which is directly bound to the central atom, may be divalent, trivalent, etc.

A list of the pentammine salts, together with complete references, will be found in the report of my lecture given before the Deutsche Chem. Gesellschaft.¹

Type
$$\left[Me_{(NH_3)_4}^{X_2}\right]X_n$$
, Diacidotetrammine salts.

When the pentammines lose a molecule of ammonia, tetrammine salts result. In these compounds two monovalent acid residues are directly linked to the central metallic atom. Should this atom be divalent, compounds with the constitutional formula $\begin{bmatrix} X_2 \\ Me(NH_3)_4 \end{bmatrix}$ are produced, i.e. they contain no acid residues which can be ionized, and their solutions consequently do not conduct electricity. If the metallic atom is trivalent, then one acid residue can be ionized, and when it is tetravalent, we have two acid ions.

The formulæ of these compounds are

$$\left[\mathbf{M}\mathbf{e}_{(\mathbf{N}\mathbf{H}_3)_4}^{\mathbf{X}_2}\right]\mathbf{X} \qquad \left[\mathbf{M}\mathbf{e}_{(\mathbf{N}\mathbf{H}_3)_4}^{\mathbf{X}_2}\right]\mathbf{X}_2$$

The number of members of this group is very large, for the possible combinations are very varied, owing to the fact that the acid residues X may all be different. Such compounds are not different in principle, since they may all be referred to the general formula.

I have already published 1 a list of diacidotetrammines of divalent elements. Examples of the type $\left[Me_{(NH_3)_4}^{X_2}\right]X_2$ are as follows:

$$\begin{bmatrix} Pt_{(NH_3)_4}^{(OH)_2} \end{bmatrix} X_2 & \begin{bmatrix} Pt_{(NH_3)_4}^{Cl_2} \end{bmatrix} X_2 & \begin{bmatrix} Pt_{(NH_3)_4}^{Br_2} \end{bmatrix} X_2 \\ \begin{bmatrix} Pt_{(NH_3)_4}^{I_2} \end{bmatrix} X_2 & \begin{bmatrix} Pt_{(NH_3)_4}^{(NO_3)_2} \end{bmatrix} X_2 & \begin{bmatrix} Pt_{(NH_3)_4}^{(NO_2)_2} \end{bmatrix} X_2 \\ \begin{bmatrix} HO \\ Cl \\ Pt(NH_3)_4 \end{bmatrix} X_2 & \begin{bmatrix} HO \\ Br \\ Pt(NH_3)_4 \end{bmatrix} X_2 & \begin{bmatrix} Cl \\ Br \\ Pt(NH_3)_4 \end{bmatrix} X_2 \\ \begin{bmatrix} Cl \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 & \begin{bmatrix} HO \\ O_3N \\ Pt(NH_3)_4 \end{bmatrix} X_2 & \begin{bmatrix} Cl \\ O_3N \\ Pt(NH_3)_4 \end{bmatrix} X_2 \\ \begin{bmatrix} Br \\ O_3N \\ Pt(NH_3)_4 \end{bmatrix} X_2 & \begin{bmatrix} I \\ O_3N \\ Pt(NH_3)_4 \end{bmatrix} X_2 \\ \begin{bmatrix} SO_4Pt_{(NH_3)_4} \end{bmatrix} X_2 & \begin{bmatrix} I \\ O_3N \\ Pt_{(NH_3)_4} \end{bmatrix} X_2 \\ \begin{bmatrix} SO_4Pt_{(NH_3)_4} \end{bmatrix} X_2 & \begin{bmatrix} I \\ O_3Pt_{(NH_3)_4} \end{bmatrix} X_2 \\ \end{bmatrix} \\ \begin{bmatrix} I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 & \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 \\ \end{bmatrix} \\ \begin{bmatrix} I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 & \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 \\ \end{bmatrix} \\ \begin{bmatrix} I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 & \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 \\ \end{bmatrix} \\ \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 & \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 \\ \end{bmatrix} \\ \begin{bmatrix} I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 & \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 \\ \end{bmatrix} \\ \begin{bmatrix} I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 & \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 \\ \end{bmatrix} \\ \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 & \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 \\ \end{bmatrix} \\ \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 & \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 \\ \end{bmatrix} \\ \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 & \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 \\ \end{bmatrix} \\ \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 & \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 \\ \end{bmatrix} \\ \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 & \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 \\ \end{bmatrix} \\ \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 & \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 \\ \end{bmatrix} \\ \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 & \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 \\ \end{bmatrix} \\ \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 & \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 \\ \end{bmatrix} \\ \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 & \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 \\ \end{bmatrix} \\ \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 & \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 \\ \end{bmatrix} \\ \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 & \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 \\ \end{bmatrix} \\ \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 & \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 \\ \end{bmatrix} \\ \begin{bmatrix} I \\ I \\ I \end{bmatrix} Pt_{(NH_3)_4} X_2 & \begin{bmatrix} I \\ I \\$$

$$\begin{bmatrix} HO \\ O_4S Pt(NH_3)_4 \end{bmatrix} X \qquad \begin{bmatrix} Br \\ O_4S Pt(NH_3)_4 \end{bmatrix} X$$

$$\begin{bmatrix} Cl \\ CO_3 Pt(NH_3)_4 \end{bmatrix} X \qquad \begin{bmatrix} Br \\ CO_3 Pt(NH_3)_4 \end{bmatrix} X$$

$$\begin{bmatrix} NO \\ CO_3 Pt(NH_3)_4 \end{bmatrix} X \qquad \begin{bmatrix} Cl \\ PO_4 Pt(NH_3)_4 \end{bmatrix}$$

$$\begin{bmatrix} Br \\ PO_4 Pt(NH_3)_4 \end{bmatrix} \qquad \begin{bmatrix} NO \\ PO_4 Pt(NH_3)_4 \end{bmatrix}$$

The great majority of these compounds have been described by Cleve. To this group also belong the nitrosohydroxotetrammin ruthene salts.2

(d) Type
$$\left[Me_{(NH_3)_3}^{X_3}\right]X_n$$
, Triacidotriammine salts.

Triammine salts, the central atom of which is tetravalent, will still have one ionic acid residue corresponding to the following formula:

$$\left[\mathbf{Me_{(\mathbf{NH_3})_3}^{X_3}}\right]\mathbf{X}$$

Examples of this type are to be found in the salts of chloro- and bromoplatinimonodiammines:

$$\left[\operatorname{Pt}^{\operatorname{Cl}_3}_{(\operatorname{NH}_3)_3}\right]$$
X and $\left[\operatorname{Pt}^{\operatorname{Br}_3}_{(\operatorname{NH}_3)_3}\right]$ X

Triammine salts containing a central atom of still higher valency are unknown.

(e) Diammine and Monoammine Salts.

Diammine and monoammine salts containing an ionic acid residue with the general formulæ:

$$\left[\mathbf{M}\mathbf{e}_{(\mathbf{N}\mathbf{H}_3)_2}^{\mathbf{X}_4}\right]\mathbf{X}_{\mathbf{n}}$$
 and $\left[\mathbf{M}\mathbf{e}_{(\mathbf{N}\mathbf{H}_3)}^{\mathbf{X}_5}\right]\mathbf{X}_{\mathbf{n}}$

are unknown.

² Werner, Ber., 40, 2614 (1907).

 ¹ Kong. Vet. Akad. Handl., 10, Nr. 93; cf. Gerhardt, Compt. rend., 1850,
 p. 373; Annalen, 76, 307 (1850); Räwsky, ibid., 68, 316 (1848); Ann. Chim.
 Phys., (3) 22, 278 (1848).

4. Compounds of the Higher Order with Carbides.

Only certain groups of carbides are able to form compounds of the higher order resembling those formed by halides, oxides, nitrides, etc. Saturated hydrocarbons are unsuited for this purpose. On the other hand, the unsaturated hydrocarbons, including benzene, form addition products of this type. But it has been possible in rare instances to give a constitution to such compounds, in spite of the fact that the carbide addition-products are comparable to those formed by amines. This is a branch of the subject which has received but little attention, and it is to be expected that research on these compounds would go far to clearing the much-discussed question of the constitution of the carbonium salts. The following examples illustrate this type of compound:

(a) Compounds with Carbon Monoxide:

Cl₂PtCO, Cl₂Pt:
$$^{CO}_{CO}$$
, (Cl₂Pt)₂(CO)₃, Cl₂Pt(COCl₂)₂, Br₂PtCO, O₄S. Cu₂(CO)₂ + H₂O.³

(b) Compounds with Hydrocarbons:

$$\begin{array}{lll} \text{Cl}_2\text{Cu}_2 \,.\, \text{C}_2\text{H}_{2},^4 & \text{Cl}_2\text{Fe} \,.\, \text{C}_2\text{H}_4 + \text{H}_2\text{O},^5 & \text{Br}_2\text{Fe} \,.\, \text{C}_2\text{H}_4 + 2\text{H}_2\text{O},^6 \\ \text{Cl}_2\text{Pt} \,.\, \text{C}_2\text{H}_4,^7 & (\text{CuCl})_6 \,.\, \text{C}_2\text{H}_2,^8 & \text{Cl}_3\text{Al} \,.\, 3\text{C}_6\text{H}_6,^9 & \text{Cl}_3\text{Al} \,.\, 3\text{C}_7\text{H}_8.^{10} \end{array}$$

- ¹ Schutzenberger, Ann. Chim. Phys., (4) 21, 350 (1870); Annalen, 8, Suppl., 242 (1868).
 - ² Pullinger, Ber., 24, 2291 (1891).
 - 3 Joannis, Compt. rend., 137, 189 (1903).
 - ⁴ Chavastelon, ibid., 126, 1810 (1898).
 - ⁶ Kachler, Ber., 2, 510 (1869).
 - ⁶ Chojnaki, Zeitsch., f. Chem., 1870, p. 420.
 - ⁷ Zeise, Pogg. Ann., 20, 497, 542; 40, 234 (1837).
 - ⁸ Hofmann and Küspert, Zeitsch. anorg. Chem., 15, 205 (1897).
- Gustavson, Ber., 11, 1251; Friedel Crafts, Ann. Chim. Phys., (6) 14, 467 (1888).
 - 10 Crafts, J. pr. Chem., (2) 42, 506 (1890).

Kondakow has described some addition compounds formed by zinc chloride and hydrocarbons. He showed that ethylene compounds formed addition products with the general formula C_nH_{2n} . $2ZnCl_{2}$.

¹ J. Russ. Phys. Chem. Soc., (1) 25, 345 (1893); J. pr. Chem., 48, 467 (1893).

The following inorganic double carbides are known:

¹ Williams, Compt. rend., 127, 483 (1898).

² Carnot and Goutal, ibid., 128, 207 (1899).

³ Moissan and Konzuetzow, ibid., 137, 292 (1903).

One addition-compound, the result of the union of an oxide and carbide, is known:

CeC2. 2CeO.1

5. Compounds of the Higher Order containing Different Molecular Components.

1. Addition Compounds.

(a) General.

Up to the present we have considered, for the sake of simplicity, only those compounds of higher order which are formed by the addition of a definite sort of molecule. But a central atom, which is able to take up several molecules, will naturally be able to take up molecular components which are chemically different. Thus, platinum chloride is able to form additions not only with two molecules of ammonia, or two molecules of a chloride RCl, but also with one of each of these groups. In this case the compound $\text{Cl}_4\text{Pt}^{NH_3}$ would be formed. It occupies a position intermediate between $\text{Cl}_4\text{Pt}^{\cdot} \overset{NH_3}{\cdot} \text{and} & \text{Cl}_4\text{Pt}^{\cdot} \overset{ClR}{\cdot} i.e.$ it is at the same time a metallic ammonium derivative and a double halide. As is obvious, the variety of compounds which could be prepared in this way is very great. In many cases the resulting compounds are of considerable interest.

(b) Transition Series between Metallic Ammino Compounds and Complex Salts.

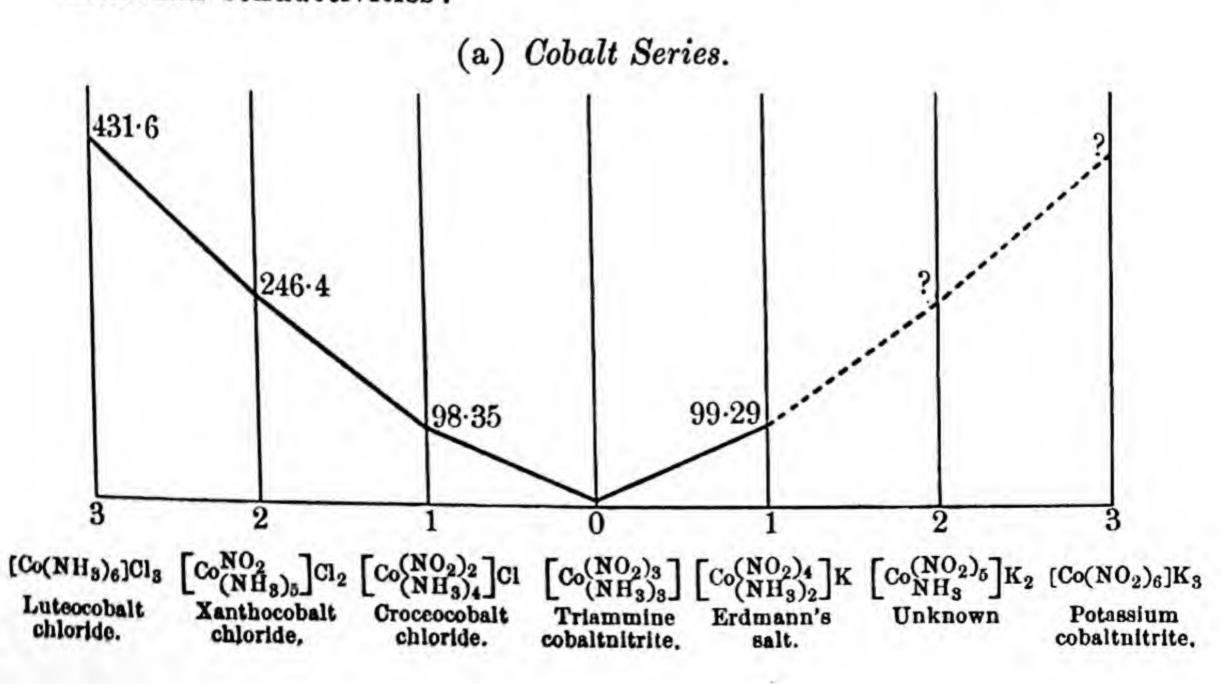
The group to which we will first direct our attention is illustrated by the above compounds. These compounds are of special interest because they are mixed compounds intermediate between the metallic ammino-compounds and the complex salts. In other words,

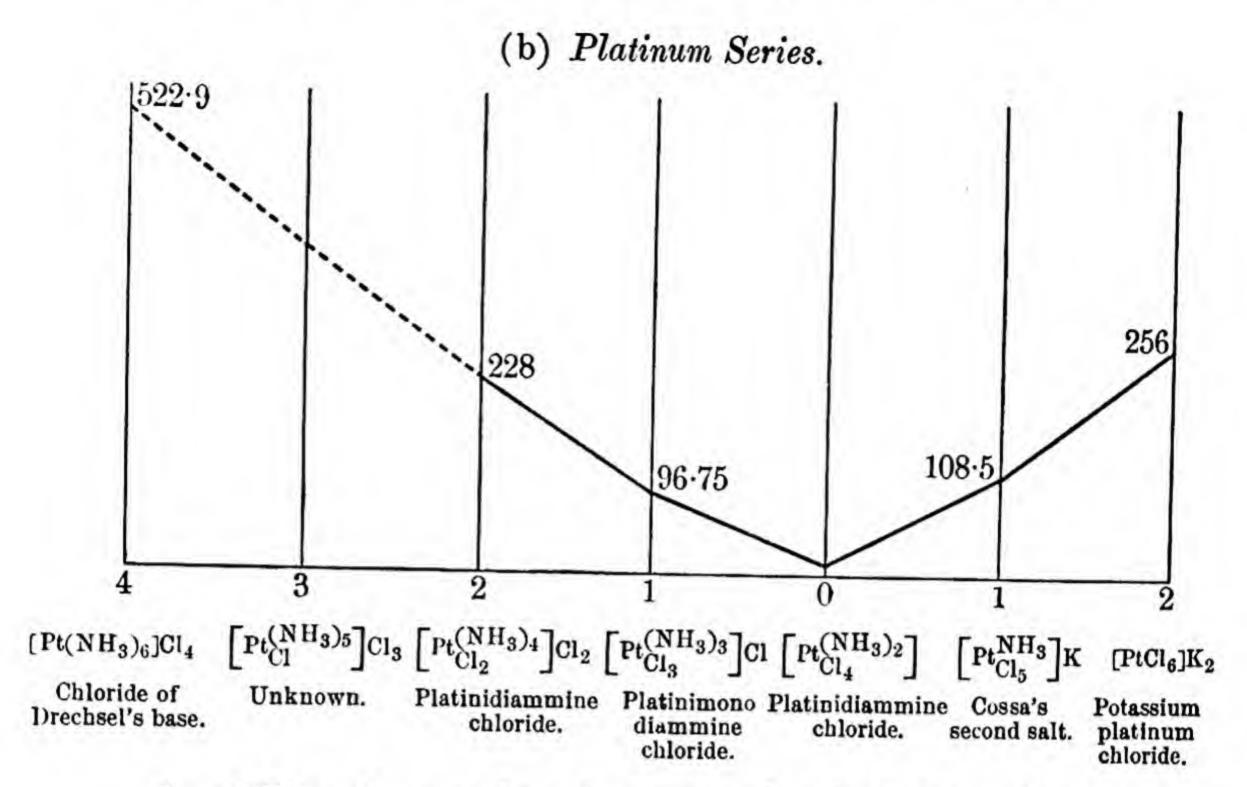
they form the middle members in the following series: (1) Metallic ammino-compounds formed by substitution; (2) metallic ammino-compounds formed by addition; (3) complex salts containing ammonia; (4) pure complex salts.

The following examples illustrate such a series:

$$\begin{bmatrix} C_0(NH_3)_6](NO_2)_3, & \begin{bmatrix} C_0(NO_2)_1\\ NH_3)_5 \end{bmatrix}(NO_3)_2, & \begin{bmatrix} C_0(NO_2)_2\\ NH_3)_4 \end{bmatrix}NO_2, \\ \begin{bmatrix} C_0(NO_2)_3\\ NH_3)_3 \end{bmatrix}, & \begin{bmatrix} C_0(NO_2)_4\\ NH_3)_2 \end{bmatrix}R, & \begin{bmatrix} C_0(NO_2)_5\\ NH_3)_2 \end{bmatrix}R_2, & \begin{bmatrix} C_0(NO_2)_6\end{bmatrix}R_3. \\ & Unknown \end{bmatrix}$$

Both the chemical and electro-chemical behaviour of these compounds is well expressed by the graphic representation of their molecular conductivities:





As additional examples of compounds which have the double character of metal ammino salts and complex salts, the following compounds may be mentioned:

$$\begin{split} & \Big[\mathrm{Pt}^{\mathrm{NH}_3}_{\mathrm{Cl}_3} \Big] \mathrm{R}, \quad \Big[\mathrm{Pt}^{\mathrm{Py}}_{\mathrm{Cl}_3} \Big] \mathrm{R}, \quad \Big[\mathrm{Pt}^{\mathrm{Py}}_{\mathrm{Cl}_5} \Big] \mathrm{R}, \quad \Big[\mathrm{Fe}^{\mathrm{NH}_3}_{\mathrm{Cy}_5} \Big] \mathrm{R}_3, \\ & \Big[(\mathrm{H}_3 \mathrm{N})_3 \mathrm{Co}^{\mathrm{Cl}_2}_{(\mathrm{NO}_2)_2} \Big] \mathrm{R}, \quad \Big[(\mathrm{H}_3 \mathrm{N})_2 \mathrm{Co}^{\mathrm{C}_2 \mathrm{O}_4}_{(\mathrm{NO}_2)_2} \Big] \mathrm{R}, \quad \Big[\mathrm{Cr}^{\mathrm{Py}_2}_{(\mathrm{SCN})_4} \Big] \mathrm{R}, \\ & \Big[\mathrm{Co}^{(\mathrm{NH}_3)_3}_{(\mathrm{C}_2 \mathrm{O}_4)_2} \Big] \mathrm{R}, \quad \Big[\mathrm{Cr}^{\mathrm{en}}_{(\mathrm{C}_2 \mathrm{O}_4)_2} \Big] \mathrm{R}. \end{split}$$

All these compounds which contain ammonia in a complex acid radicle expose the inaccuracy of Abegg and Bodländer's opinion, viz. that it is impossible for ammonia to be a constituent of a complex acid radicle.

(c) Transition Series between Hydrates and Complex Salts.

Compounds occupying a position intermediate between the hydrates on the one hand and complex salts on the other, are formed when a binary compound takes up at the same time both water and a simple salt. Since most inorganic compounds are prepared in aqueous solution, it is easy to understand why it is that most inorganic compounds belong to this group. Examples of such compounds are:

$$\begin{bmatrix} O \\ VF_{3} \\ OH_{2} \end{bmatrix} Zn + 6H_{2}O,^{1} \begin{bmatrix} O_{2} \\ WF_{3} \\ OH_{2} \end{bmatrix} (NH_{4})_{2},^{2} \begin{bmatrix} O_{2} \\ MoF_{3} \\ OH_{2} \end{bmatrix} K_{2},^{3}$$

$$\begin{bmatrix} MoF_{3} \\ OH_{2} \end{bmatrix} K,^{3} \begin{bmatrix} MoF_{3} \\ OH_{2} \end{bmatrix} NH_{4},^{3} \begin{bmatrix} MnF_{5} \\ OH_{2} \end{bmatrix} K_{2},^{4} \begin{bmatrix} CrF_{5} \\ OH_{2} \end{bmatrix} K_{2},^{5}$$

$$\begin{bmatrix} CrCl_{5} \\ OH_{2} \end{bmatrix} R_{2},^{6} \begin{bmatrix} FeCl_{5} \\ OH_{2} \end{bmatrix} K_{2},^{7} \begin{bmatrix} AlCl_{5} \\ OH_{2} \end{bmatrix} K_{2},^{7} \begin{bmatrix} RhCl_{5} \\ OH_{2} \end{bmatrix} K_{2},^{8}$$

$$\begin{bmatrix} CoF_{4} \\ OH_{2} \end{bmatrix} (NH_{4})_{2},^{9} \begin{bmatrix} FeF_{4} \\ OH_{2} \end{bmatrix} K_{2},^{9} \begin{bmatrix} SnBr \\ OH_{2} \end{bmatrix} (NH_{4})_{2},^{10}$$

$$\begin{bmatrix} FeCN_{5} \\ OH_{2} \end{bmatrix} Na_{3} + 6H_{2}O,^{11} \text{ etc.}$$

Werner, Zeitsch. anorg. Chem., 9, 386 (1895).

² Marignac, Ann. Chim. Phys., (3) 69, 65 (1863).

³ Delafontaine, Arch. Sc. phys. nat., 30, 240.

⁴ Christensen, J. pr. Chem., (2) 35, 57, 161 (1887).

⁵ Christensen, ibid., (2) 35, 168 (1887).

⁶ Werner and Gubser, Ber., 34, 1579 (1901).

¹ Christensen, J. pr. Chem., (2) 35, 161 (1887).

⁸ Seubert and Kobbe, Ber., 23, 2557 (1890).

Wagner, ibid., 19, 896 (1886).

Raymann and Preis, Jahresb., 1884, p. 436; Annalen, 223, 323 (1883).

11 Hofmann, Annalen, 312, 1 (1900).

The following transition series of compounds between a hydrate and a complex salt is theoretically possible.

$$\begin{split} & X_{2} Me(OH_{2})_{4}, \quad \left[Me_{(OH_{2})_{3}}^{X_{3}}\right]R, \quad \left[Me_{(OH_{2})_{2}}^{X_{4}}\right]R_{2}, \quad \left[Me_{OH_{2}}^{X_{5}}\right]R_{3}, \\ & \left[MeX_{6}\right]R_{4}; \quad Me_{(OH_{2})_{3}}^{X_{3}}, \quad \left[Me_{(OH_{2})_{2}}^{X_{4}}\right]R, \quad \left[Me_{(OH_{2})_{2}}^{X_{5}}\right]R_{2}, \quad \left[MeX_{6}\right]R_{3}; \\ & \left[Me_{(OH_{2})_{2}}^{X_{4}}\right], \quad \left[Me_{OH_{2}}^{X_{5}}\right]R, \quad \left[MeX_{6}\right]R_{2}. \end{split}$$

For the last two transition series actual examples are known:

$$\begin{array}{lll} v_{(OH_2)_3}^{F_3}, & \left[v_{(OH_2)_2}^{F_4}\right]_{NH_4}, & \left[v_{(OH_2)}^{F_5}\right]_{(NH_4)_2}, & (VF_6)(NH_4)_3, \\ & Pt_{(OH_2)_2}^{Cl_4}, & \left[Pt_{OH_2}^{Cl_5}\right]_{H_4}, & (PtCl_6)H_2. \end{array}$$

Amongst complex salts which contain water there is still very much that is not clear, and in order to clear up finally the constitutions of many of the compounds belonging to this class, new experimental methods will have to be discovered.

(d) Further Examples of Compounds formed by the Simultaneous Addition of Different Types of Molecules.

An addition compound containing at the same time both water and ammonia has been prepared by Nordenskjöld:1

$$(NCS)_2Cr_{OH_2}^{(NH_3)_2} + H_2O$$

I have had this compound examined lately, and it appears that it is to be considered as an oxonium salt with the following formula:

$$\left[(\mathrm{NCS})_{\scriptscriptstyle{3}} \mathrm{Cr}_{\mathrm{OH}}^{(\mathrm{NH_{3}})_{\scriptscriptstyle{2}}} \right] \mathrm{H} \cdot \mathrm{OH_{2}}$$

for it is possible to prepare a series of salts from organic bases with the general formula:2

$$\left[(\mathrm{NCS})_3 \mathrm{Cr}_{\mathrm{OH}}^{(\mathrm{NH_3})_2} \right] \mathrm{H} \cdot \mathrm{R}$$

Carbides, together with other components, can also take part in the formation of such compounds, e.g.

(a) Compounds with Carbon Monoxide:

$$\begin{bmatrix} Fe_{Cy_{5}}^{CO} \end{bmatrix} R_{3}, \ [Pt_{Cl_{3}}^{CO}] R, \ [Pt_{Br_{3}}^{CO}] R, \ [Pt_{I_{3}}^{CO}] R, \ [Pt_{(SCN)_{3}}^{CO}] R,^{3} \\ Cl_{2}Pt_{(NH_{3})_{2}}^{CO}, \ [Pt_{(NH_{3})_{2}}^{(CO)_{2}}] Cl_{2}^{4} \ Cl_{2}Pt_{Py}^{CO}, \ Br_{2}Pt_{Pv}^{CO},^{CO} \\ Cl_{2}Pt_{NH_{2}}^{CO}, \ NHC_{6}H_{5}^{.5} \end{bmatrix}$$

- ³ Mylius and Förster, Ber., 24, 2424 (1891).
- ⁴ Schützenberger, Bull. Soc. Chim., (2) 14, 87 (1870).
- ⁵ Förester, Ber., 24, 375 (1891).

(b) Alkylene Compounds:

$$\begin{split} & \Big[\mathrm{Pt}^{\mathrm{C}_{2}\mathrm{H}_{4}}_{\mathrm{Cl}_{3}} \Big] \mathrm{R}, \quad \Big[\mathrm{Pt}^{\mathrm{C}_{2}\mathrm{H}_{4}}_{\mathrm{Br}_{3}} \Big] \mathrm{R}, \quad \Big[\mathrm{Pt}^{\mathrm{C}_{3}\mathrm{H}_{8}}_{\mathrm{Cl}_{3}} \Big] \mathrm{R}, \quad \Big[\mathrm{Pt}^{\mathrm{C}_{5}\mathrm{H}_{10}}_{\mathrm{Cl}_{3}} \Big] \mathrm{R} \\ & \Big[\mathrm{Ir}^{\mathrm{C}_{2}\mathrm{H}_{4}}_{\mathrm{Cl}_{3}} \Big] \mathrm{R}, \quad \Big[\mathrm{Ir}^{\mathrm{C}_{2}\mathrm{H}_{4}}_{\mathrm{Cl}_{4}} \Big] \mathrm{R}_{2}. \\ & \mathrm{Cl}_{4} \mathrm{Pt}^{\mathrm{C}_{2}\mathrm{H}_{4}}_{\mathrm{(PCl}_{3)_{2}}}, \quad \mathrm{Cl}_{2} \mathrm{Pt}^{\mathrm{C}_{2}\mathrm{H}_{4+1}}_{\mathrm{NH_{3}}} \\ & \mathrm{Cl}_{2} \mathrm{Pt}^{\mathrm{C}_{2}\mathrm{H}_{4}}_{\mathrm{NH_{2}}\mathrm{C}_{6}\mathrm{H_{5}}}, \quad \mathrm{Cl}_{2} \mathrm{Pt}^{\mathrm{C}_{2}\mathrm{H}_{4}}_{\mathrm{NH}(\mathrm{C}_{2}\mathrm{H_{5}})_{2}}, \quad \mathrm{Cl}_{2} \mathrm{Pt}^{\mathrm{C}_{2}\mathrm{H_{4}}}_{\mathrm{NH_{2}}, \mathrm{CH_{2}}, \mathrm{CH_{2}}, \mathrm{CH_{2}}, \\ & \mathrm{Cl}_{2} \mathrm{Pt}^{\mathrm{C}_{2}\mathrm{H_{4}}}_{\mathrm{NH_{2}}\mathrm{C}_{6}\mathrm{H_{5}}}, \quad \mathrm{Cl}_{2} \mathrm{Pt}^{\mathrm{C}_{2}\mathrm{H_{4}}}_{\mathrm{NH}(\mathrm{C}_{2}\mathrm{H_{5}})_{2}}, \quad \mathrm{Cl}_{2} \mathrm{Pt}^{\mathrm{C}_{2}\mathrm{H_{4}}}_{\mathrm{NH_{2}}, \mathrm{CH_{2}}, \mathrm{CH_{2}}, \\ & \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \\ & \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \\ & \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \\ & \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \\ & \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \\ & \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \\ & \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \\ & \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \\ & \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \\ & \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \\ & \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \\ & \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \\ & \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \\ & \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \\ & \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \\ & \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \\ & \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \\ & \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \\ & \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \\ & \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \\ & \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \quad \mathrm{CH_{2}}, \\ & \mathrm{CH_$$

- ¹ Zeise, Pogg. Ann., 21, 497 (1831); 40, 234 (1837).
- ² Griess and Martius, Annalen, 120, 324 (1861).

¹ Zeitsch. anorg. Chem., 1, 126 (1892).

² A. Siemssen, Inaug. Dissertation, Zürich (1909).

A very peculiar group of addition compounds exists of which the first representative, nickelcyanidebenzeneammonium, $Cy_2Ni\frac{N}{C_6H_6}$, was discovered by Hofmann and Küspert. Hofmann and Arnoldi re-examined it and described it in greater detail. Moreover, they were able to prepare other addition-products analogous to the first compound, which contained aniline, phenol, pyridine, pyrrol, thiophene, and furfuran.

It is quite a common thing to have different salts unexpectedly combine together to form a complex. Hofmann 3 noted this peculiarity when working on the ferrocyanides and has described the following compounds:

$$\begin{array}{cccc} Cy_{2}Fe_{\left(NO_{2}Na\right)_{3}}^{\left(CyNa\right)_{3}} & Cy_{2}Fe_{NO_{2}C_{n}H_{2n+1}}^{\left(CyH\right)_{3}} & Cy_{2}Fe_{SO_{3}Na_{2}}^{\left(CyNa\right)_{3}} \\ & Cy_{2}Fe_{\left(AsO_{3}H_{2}Na\right)}^{\left(CyNa\right)_{3}} & \end{array}$$

That it is possible for three or four components to be taken up by a central atom, when the auxiliary valencies on the latter are sufficient in number, is obvious and requires no further discussion. Nevertheless compounds of this description have received hardly any attention from experimenters.

2. Substitution Compounds. Aquometalammino Salts.

Ammonia and water behave similar to one another in the formation of substitution compounds. It is to be expected, therefore, that they can take part simultaneously in the formation of substitution compounds. This anticipation is confirmed by experiment, and the compounds which result from the simultaneous substitution of water and ammonia are known as aquometallicammino-compounds. They are a particularly important class, because they permit the functional signification of the water to be disclosed in a very suggestive manner. The series of compounds which are prepared from the hexammines by the substitution of one or two molecules of ammonia by water are called the aquo-

¹ Zeitsch. anorg. Chem., 15, 206 (1897).

Ber., 39, 339 (1906).
 Zeitsch. anorg. Chem., 12, 167 (1896).

pentammines (pentamminroseo salts) and the diaquopentammines (tetramminroseo salts):

$$\begin{bmatrix} \text{Co}_{(\text{NH}_3)_5}^{\text{OH}_2} \end{bmatrix} X_3^{\ 1} & \begin{bmatrix} \text{Cr}_{(\text{NH}_3)_5}^{\text{OH}_2} \end{bmatrix} X_3^{\ 2} \\ \begin{bmatrix} \text{Rh}_{(\text{NH}_3)_5}^{\text{OH}_2} \end{bmatrix} X_3^{\ 3} & \begin{bmatrix} \text{Co}_{(\text{NH}_3)_4}^{(\text{OH}_2)_2} \end{bmatrix} X_3^{\ 4} \end{bmatrix}$$

¹ Jörgensen, J. pr. Chem., (2) 31, 49 (1885).

² Christensen, ibid., (2) 23, 26 (1881).

³ Jörgensen, ibid., (2) 34, 394 (1886).

4 Jörgensen, Zeitsch. anorg. Chem., 2, 279 (1892).

In these salts the water plays exactly the same rôle as is played by ammonia in the metallic ammino-complexes, i.e. the exit of each molecule of water from the complex causes an acid residue to lose its ionic properties. In this way the aquopentammine chlorides of cobalt and chromium by loss of water are transformed into chloropentammine chlorides:

$$\begin{bmatrix} Co_{(NH_3)_5}^{OH_2} \end{bmatrix} Cl_3 = \begin{bmatrix} Co_{(NH_3)_5}^{Cl} \end{bmatrix} Cl_2 + H_2O$$

$$\begin{bmatrix} Cr_{(NH_3)_5}^{OH_2} \end{bmatrix} Cl_3 = \begin{bmatrix} Cr_{(NH_3)_5}^{Cl} \end{bmatrix} Cl_2 + H_2O$$

These examples bring out very clearly the complete agreement in the functions of water and ammonia, for hexammine chlorides on losing one molecule of ammonia produce chloropentammine chlorides:

$$\left[\operatorname{Cr_{(NH_3)_5}^{NH_3}}\right]\operatorname{Cl_3} = \left[\operatorname{Cr_{(NH_3)_5}^{Cl}}\right]\operatorname{Cl_2} + \operatorname{NH_3}$$

Aquopentammincobalt- and chromiumbromides, aquopentamminchromium iodide and aquopentammincobalt nitrate all behave similarly to aquopentammin chloride. Through the loss of water are produced bromopentammincobalt and chromium bromides, iodopentamminchromium iodide and nitratopentammincobalt nitrate. Further, the action of nitrous acid on these aquosalts produces nitropentammine salts, the action of thiocyanic acid produces thiocyanopentammine salts, etc.

We can sum up, therefore, the behaviour of these salts in the following words: through loss of water by the aquopentammines it is possible for the most varied acid residues to become directly bound to the central metallic atom:

$$\[Me_{(NH_3)_5}^{OH_2} \] X_3 = \[Me_{(NH_3)_5}^{X} \] X_2 + H_2O$$

Polyvalent acid residues, such as sulphuric acid, oxalic acid, sulphurous acid, carbonic acid, etc., also exhibit this behaviour.

From the diaquotetrammincobalt salts, in which all the acid residues are in the ionic condition, through loss of a molecule of water are produced acidoaquotetrammine salts. In these salts an acid residue is linked directly to the positive complex, and through loss of both molecules of water diacidotetrammine salts result in which only one acid residue has ionogene properties:

$$\begin{bmatrix} H_2O \\ H_2O \end{bmatrix} CO(NH_3)_4 \end{bmatrix} Cl_3 = \begin{bmatrix} Cl \\ H_2O \end{bmatrix} CO(NH_3)_4 \end{bmatrix} Cl_2 + H_2O$$

$$\begin{bmatrix} H_2O \\ Cl \end{bmatrix} CO(NH_3)_4 \end{bmatrix} Cl_2 = \begin{bmatrix} Cl \\ Cl \end{bmatrix} CO(NH_3)_4 \end{bmatrix} Cl_2 + 2H_2O$$

Beyond the hydrated tetrammines already mentioned the following have been prepared:

$$\begin{bmatrix} O_2N \\ H_2O \\ Co(NH_3)_4 \end{bmatrix} X_{2,^1} \quad \begin{bmatrix} Br \\ H_2O \\ Co(NH_3)_4 \end{bmatrix} X_{2,^2} \quad \begin{bmatrix} H_2O \\ H_2O \\ Co \\ en_2 \end{bmatrix} X_{3,^3}$$
 in two isomeric series,

$$\begin{bmatrix} \mathbf{Cl} \\ \mathbf{H_2O} \mathbf{Cr(NH_3)_4} \end{bmatrix} \mathbf{X_2,^4} \quad \begin{bmatrix} \mathbf{H_2O} \\ \mathbf{H_2O} \mathbf{Cr(NH_3)_4} \end{bmatrix} \mathbf{X_3,^5}$$

1 Jörgensen, Zeitsch. anorg. Chem., 7, 290 (1894).

² Werner and Wolberg, Ber., 38, 2009 (1905).

Werner, Zeitsch. anorg. Chem., 19, 1645 (1899).
 Cleve, Vet. Akad. Handl., 6, No. 4, 6 (1865); Jörgensen, J. pr. Chem., (2)
 42, 206 (1886).

⁵ Pfeiffer, Ber., 40, 3126 (1907).

and in every instance it has been shown that the water molecules have the same signification with respect to the acid residues as in the above examples.

But in the hexammines it is possible to substitute for ammonia more than two molecules of water. Thus the following triammin-cobalt salts are known:

$$\label{eq:continuous} \begin{split} & \text{[Cl}_3\text{Co}(NH_3)_3\text{], } \left[\text{Cl}_2\text{Co}_{(NH_3)_3}^{OH_2}\right] \text{Cl, } \left[\text{ClCo}_{(NH_3)_3}^{(OH_2)_2}\right] \text{Cl}_2, \\ & \left[\text{Co}_{(NH_3)_3}^{(OH_2)_3}\right] \text{Cl}_3 \end{split}$$

Every molecule of water in these compounds has exactly the same functions as ammonia in the metallic ammino-complexes. Hence, the entrance or the exit of a molecule of water causes a change in the functions of the acid residue.

¹ Vortmann, Ber., 10, 1451 (1877); 15, 1890 (1882); 22, 2648 (1889). Cf. Jörgensen, J. pr. Chem., (2) 42, 206 (1886).

No:--

Of the three chlorine atoms in the trihydrates all three have ionic properties, in the dihydrates only two, in the monohydrates one, and in the anhydrous salts none. For the question of the existence of hydrates in solution it is of importance to note that all three hydrates yield characteristic solutions, from which they can be obtained again quite unaltered. The trihydrate gives a purple-coloured solution. The dihydrate a reddish-blue, and the monohydrate a bluish-green, and every one of these solutions exhibits its characteristic reactions. It cannot be doubted, therefore, that each hydrate preserves its individuality in solution.

Other triammine salts, in which water clearly exercises a similar function are the following:

$$\begin{bmatrix} Cl_{2}Co_{NH_{3}}^{OH_{2}} \\ Cl_{1}^{1} & \begin{bmatrix} Cl_{1}Co_{(NH_{3})_{3}}^{OH_{2}} \\ Br_{1}^{OH_{2}} \end{bmatrix}Br_{,1}^{1} & \begin{bmatrix} Cl_{2}Co_{NH_{3}}^{OH_{2}} \\ Br_{2}Co_{NH_{3}}^{OH_{3}} \end{bmatrix}Br_{,1}^{1} \\ \begin{bmatrix} Cl_{1}Co_{NH_{3}}^{OH_{2}} \\ Br_{1}^{OH_{2}} \end{bmatrix}Br_{,2}^{2} & \begin{bmatrix} Cl_{1}Co_{NH_{3}}^{OH_{2}} \\ El_{2}^{OH_{2}} \end{bmatrix}Cl_{2}Ol_{4}^{1} \end{bmatrix} \end{bmatrix} Cl_{2}Ol_{4}^{1}$$

¹ Werner and Grün, Ber., 38, 4033 (1905).

² Werner and Grün (Grün, Dissertation, Zurich, 1901).

These compounds, however, have not yet been exhaustively examined.

The preparation of a complete transition series from the cobalt ammino-compounds to the hexhydrates of trivalent cobalt is defeated owing to the instability of the water linkings in the higher hydrates. On the other hand, chromium has yielded such a series. For, with only one member missing, it has been found possible to prepare all the compounds between chromium hexammine chloride and the blue hydrate of chromium chloride: 1

$$\begin{split} & \big[\mathrm{Cr}(\mathrm{NH_3})_6 \big] \mathrm{Cl_3}, & \Big[\mathrm{Cr}_{(\mathrm{NH_3})_5}^{\mathrm{OH_2}} \big] \mathrm{Cl_3}, & \Big[\mathrm{Cr}_{(\mathrm{NH_3})_4}^{(\mathrm{OH_2})_2} \big] \mathrm{Cl_3}, \\ & \Big[\mathrm{Cr}_{(\mathrm{NH_3})_3}^{(\mathrm{OH_2})_3} \big] \mathrm{Cl_3}, & \Big[\mathrm{Cr}_{(\mathrm{NH_3})_2}^{(\mathrm{OH_2})_4} \big] \mathrm{Cl_3}, & \Big[\mathrm{Cr}_{(\mathrm{NH_3})_2}^{(\mathrm{OH_2})_5} \big] \mathrm{Cl_3}. \end{split}$$

The only compound, therefore, which is missing is:

$$\left[\mathrm{Cr_{NH_{3}}^{(\mathrm{OH_{2}})_{5}}}\right]\mathrm{Cl_{3}}$$

All the compounds in this series contain three ionic chlorine atoms, and consequently silver nitrate, when added to a freshly

¹ Werner, Ber., 39, 2656 (1906).

prepared solution of the salt, immediately precipitates all the chlorine. The function of the water in these compounds is similar to that of the water in the aquo-salts of the ammonium compounds of cobalt, i.e. the loss of water by the complex requires a chlorine ion to lose its ionic properties.

When aquopentammine chromium chloride loses a molecule of water chloropentammine chromium chloride results:

$$\left[\mathrm{Cr_{(NH_3)_5}^{OH_2}}\right]\mathrm{Cl_3} = \left[\mathrm{Cr_{(NH_3)_5}^{Cl}}\right]\mathrm{Cl_2} + \mathrm{H_2O}$$

and when the diaquotetrammine chloride gives up one water molecule, chloroaquotetramminechromium chloride is produced:

$$\begin{bmatrix} \mathbf{H}_2\mathbf{O} \\ \mathbf{H}_2\mathbf{O} \end{bmatrix} \mathbf{Cr}(\mathbf{NH}_3)_4 \end{bmatrix} \mathbf{Cl}_3 \ = \ \begin{bmatrix} \mathbf{Cl} \\ \mathbf{H}_2\mathbf{O} \end{bmatrix} \mathbf{Cr}(\mathbf{NH}_3)_4 \end{bmatrix} \mathbf{Cl}_2 \ + \ \mathbf{H}_2\mathbf{O}$$

The behaviour of the last three members of the above series is peculiar, for all lose two molecules of water very easily, thus yielding compounds in which only one chlorine is ionic:

$$\begin{split} \big[(H_2O)_3 Cr(NH_3)_3 \big] Cl_3 &= \Big[Cl_2 Cr_{(NH_3)_3}^{OH_2} \Big] Cl + 2H_2O \\ \big[(H_2O)_4 Cr(NH_3)_2 \big] Cl_3 &= \Big[Cl_2 Cr_{(NH_3)_2}^{(OH_2)_2} \Big] Cl + 2H_2O \\ \big[Cr(OH_2)_6 \big] Cl_3 &= \big[Cl_2 Cr(OH_2)_4 \big] Cl + 2H_2O \\ \end{split}$$

The blue hexadydrate of chromium behaves exactly analogously to the hydrated chromium ammino-complexes, and the same thing is true of the hexahydrate of chromium bromide. It only remains to be mentioned that all these hydrates preserve their individuality in solution.

(b) Compounds produced by the Substitution of Halides and Analogous Compounds.

The consideration of the substitution compounds has shown that the most diverse chemical compounds can take part in the formation of substitution complexes, e.g. ammonia, amines, water, alcohol, ketones, esters of carbonic acid, organic acids, metallic hydroxides, metallic salts, etc. It is to be expected, therefore, that in general all compounds, which are able to produce auxiliary valencies, are able to take part, as far as their nature permits, in the formation of substitution compounds.

When determining the constitution of many compounds it is

important to know that simple salts as halides, thiocyanides, nitrites, etc., can also act as components of substitution compounds. The following constitutional formulæ illustrate the truth of this statement, and at the same time throw light upon the nature of the resulting compounds:

$$\begin{bmatrix} \text{Co}_{(NH_3)_5}^{\text{NCSAg}} \end{bmatrix} (\text{NO}_3)_3,^1 & \begin{bmatrix} \text{AgNCS}_{\text{Co}(NH_3)_4} \end{bmatrix}_{\text{NO}_3}^{\text{Cl}},^2 \\ \begin{bmatrix} \text{KO}_2\text{N}_2\text{Co}(\text{NH}_3)_4 \end{bmatrix} (\text{NO}_3)_2,^3 & \begin{bmatrix} \text{CsCl}_{\text{Cr}}(\text{OH}_2)_4 \end{bmatrix} \text{Cl}_3,^4 \\ \begin{bmatrix} \text{AgCl}_{\text{Cl}}^{\text{Co}(\text{NH}_3)_4} \end{bmatrix} \text{SO}_4,^5 & \begin{bmatrix} \text{AgCl}_{\text{Co}(\text{NH}_3)_3} \end{bmatrix} \text{SO}_4,^6 \\ \end{bmatrix} \begin{bmatrix} \text{HCl}_{\text{Cl}}^{\text{Co}} \text{en}_2 \end{bmatrix} \text{Cl}_2 + 2\text{H}_2\text{O},^7 \text{ etc.} \end{bmatrix}$$

- ¹ Werner, Zeitsch. anorg. Chem., 22, 91 to 157 (1899).
- ² Werner, ibid.
- ³ Jörgensen, ibid., 17, 473 (1898).
- Werner, Ber., 34, 1602 (1901).
- ⁵ Werner, Zeitsch. anorg. Chem., 14, 31 (1897).
- ⁶ Werner, ibid., 15, 155 (1897).
- ⁷ Jörgensen, J. pr. Chem., (2) 39, 24 (1889).

Many of these compounds are produced by the addition of new components to complexes which are already co-ordinatively saturated:

$$\left[{\rm Co_{(NH_3)_5}^{NCS}}\right]\!({\rm NO_3})_2 + {\rm RNO_3} = \left[{\rm Co_{(NH_3)_5}^{NCS}}\right]\!({\rm NO_3})_3$$

These new compounds are perfectly stable, if R, which is linked to the acid residue on the central atom, be undissociated in aqueous solution. This is the case in the silver salt:

$$\left[\mathrm{Co_{(NH_3)_5}^{NCSAg}}\right](\mathrm{NO_3)_3}$$

for hydrochloric acid is without effect on its aqueous solution. If, on the other hand, R can be dissociated, then the complex will break upon solution according to the equation:

$$(O_3N)_2[(H_3N)_4Co_{NO_2}^{NO_2K}] \rightarrow [Co_{(NH_3)_4}^{(NO_2)_2}]NO_3 + \overset{+}{K} + \overset{-}{NO_3}$$

and the salt behaves like a loose addition product of a co-ordinatively saturated compound. The composition of such compounds is often used as an argument against the hypothesis of co-ordination, because they are apparently in opposition to it. Let us suppose that in the formula $(MeA_6)X_3$ all the radicles A are substituted by

halides, we get, therefore, the compound $[Me(XR)_6]X_3$, which contains three molecules XR more than corresponds to the limiting type, $X_3Me(XR)_3$, of the addition compounds. As a matter of fact, such compounds do not belong to those formed by addition, but rather to the substitution complexes, and in this way the apparent contradiction is to be explained.

Weinland and Schmidt 1 prepared a compound, the composition of which appeared to be in contradiction to the co-ordination hypothesis. Antimony chloride not only gives the salt (SbCl₆)R, but also (SbCl₇)R₂. While the chlorine in the former complies with the required co-ordination number, *i.e.* 6, that in the latter appears to be too great. These experimenters, however, were able to show that the first salt contained no ionic chlorine, whereas the latter gave a precipitate with silver chloride, and hence contained chlorine in indirect linking with antimony. The salt, consequently, must have the following constitution:

It has also been shown that the salts SbCl₇Mg + 9H₂O and SbCl₈Fe + 8H₂O contain six atoms of chlorine which cannot be precipitated by silver nitrate, and hence must be formulated as follows:

Similar reactions have led to formulating the compound

$$\left[\mathrm{Cr_{(OH_2)_4}^{Cl_2}}\right]$$
Cl + 2CsCl

thus

$$\begin{bmatrix} \text{ClCs} \\ \text{CrClCs} \\ (\text{OH}_2)_4 \end{bmatrix} \text{Cl}_3$$

For only three-fifths of the chlorine can be directly precipitated.

Additional examples of such compounds are to be found in the following list:

$$\begin{bmatrix} As_{\mathbf{F_4}}^{(\mathbf{FK})_2} \end{bmatrix} \mathbf{F} + \mathbf{H_2O,^1} \quad \begin{bmatrix} Sb^{(\mathbf{BrHChin.})_2} \\ Br_4 \end{bmatrix} Br,^2 \quad \begin{bmatrix} Sb^{(\mathbf{BrHPy})_2} \\ Br_4 \end{bmatrix} Br,^3$$

1 Marignac, Annalen, 145, 249 (1868).

² Rosenheim and Stellman, Ber., 34, 3378 (1901).

3 Ibid.

¹ Zeitsch. anorg. Chem., 44, 41 (1905).

$$\begin{bmatrix} \operatorname{Sb}^{\left[\operatorname{BrH} \cdot \operatorname{C}_{6} \operatorname{H}_{5} \operatorname{N}(\operatorname{CH}_{3})_{3}\right]_{2}} \end{bmatrix} \operatorname{Br},^{1} & \left[\operatorname{Sb}^{\left(\operatorname{ClHChin},\right)_{2}} \right] \operatorname{Cl} + \operatorname{H}_{2} \operatorname{O},^{2} \\ \left[\operatorname{Sb}^{\left(\operatorname{BrHAnil},\right)_{4}} \right] \operatorname{Br} + \operatorname{H}_{2} \operatorname{O},^{3} & \left[\operatorname{Sb}^{\left(\operatorname{BrHp-Toluid},\right)_{4}} \right] \operatorname{Br},^{4} \\ \left[\operatorname{Sb}^{\left(\operatorname{INH}_{4}\right)_{4}} \right] \operatorname{I} + 3\operatorname{H}_{2} \operatorname{O},^{5} & \left[\operatorname{Sb}^{\left(\operatorname{IHAnil},\right)_{4}} \right] \operatorname{I},^{6} & \left[\operatorname{Bi}^{\left(\operatorname{IK}\right)_{4}} \right] \operatorname{I},^{7} \\ \left[\operatorname{BiH}^{\left(\operatorname{IK}\right)_{4}} \right] \operatorname{I}_{2},^{8} & \left[\operatorname{Bi}^{\left(\operatorname{INH}_{4}\right)_{4}} \right] \operatorname{I} + 3\operatorname{H}_{2} \operatorname{O},^{9} & \left[\operatorname{Sb}^{\left(\operatorname{FK}\right)_{2}} \right] \operatorname{F} + 2\operatorname{H}_{2} \operatorname{O},^{10} \\ \left[\operatorname{Sb}^{\left(\operatorname{FNH}_{4}\right)_{4}} \right] \operatorname{F} + 1_{\frac{1}{2}} \operatorname{H}_{2} \operatorname{O},^{11} & \left[\operatorname{Nb}^{\left(\operatorname{FK}\right)_{2}} \right] \operatorname{F},^{12} & \left[\operatorname{NbO}^{\left(\operatorname{FK}\right)_{3}} \right] \operatorname{F},^{13} \\ \left[\operatorname{Sb}^{\left(\operatorname{FNH}_{4}\right)_{3}} \right] \operatorname{F},^{14} & \left[\operatorname{Ta}^{\left(\operatorname{FNa}\right)_{2}} \right] \operatorname{F} + \operatorname{H}_{2} \operatorname{O},^{15} & \left[\operatorname{Ta}^{\left(\operatorname{FK}\right)_{2}} \right] \operatorname{F},^{16} \\ \left[\operatorname{Ta}^{\left(\operatorname{FNH}_{4}\right)_{3}} \right] \operatorname{F},^{17} & \left[\operatorname{Th}^{\left(\operatorname{ClCs}\right)_{3}} \right] \operatorname{Cl} + \operatorname{H}_{2} \operatorname{O},^{18} & \left[\operatorname{Zr}^{\left(\operatorname{FK}\right)_{3}} \right] \operatorname{F},^{19} \\ \left[\operatorname{Zr}^{\left(\operatorname{FNH}_{4}\right)_{3}} \right] \operatorname{F},^{20} & \left[\operatorname{Si}^{\left(\operatorname{FNH}_{4}\right)_{3}} \right] \operatorname{F},^{21} & \left[\operatorname{Ti}^{\left(\operatorname{FNH}_{4}\right)_{3}} \right] \operatorname{F},^{22} \\ \left[\operatorname{Ti}^{\left(\operatorname{ClHAnil}\right)_{4}} \right] \operatorname{Cl}_{2},^{23} & \left[\operatorname{Ti}^{\left(\operatorname{FNa}\right)_{3}} \right] \operatorname{F}_{2},^{24} & \left[\operatorname{Sn}^{\left(\operatorname{ClHAnil}\right)_{4}} \operatorname{Cl}_{2},^{25} \right] \operatorname{Cl}_{2},^{25} \\ \end{array}$$

- 1 Ibid.
- ² Weinland and Schmid, Zeitsch. anorg. Chem., 44, 137 (1905).
- ³ Higbee, Amer. Chem. J., 23, 150 (1900).
- 4 Ibid.
- ⁵ Niklès, Compt. rend., 51, 1097 (1860).
- 6 Higbee, loc. cit.
- ⁷ Arppe, Pogg. Ann., 64, 237 (1845).
- ⁹ Arppe, ibid.; Niklès, Compt. rend., 50, 872 (1860); Linau, Pogg. Ann., 111, 240 (1860).

8 Ibid.

- 10 Marignac, Annalen, 145, 239 (1868).
- 11 Ibid.
- · 12 Santensson, Bull. Soc. Chim., (2) 24, 53 (1875).
 - 13 Baker, Trans., 35, 760 (1879).
 - 14 Ibid.
 - 15 Marignac, Ann. Chim. Phys., (4) 9, 268 (1866).
- 16 Ibid. 17 Ibid.
- ¹⁸ Wells and Willis, Amer. J. Sci., Silliman, (4) 12, 191 (1901); Chem. Zentr., 1901, II., p. 844.
 - 19 Franz, Ber., 1870, p. 58; Marignac, J. pr. Chem., 80, 137 (1860).
 - ²⁰ Marignac, ibid., 80, 426 (1860); Jahresber., 1860, p. 137.
 - ²¹ Dammer, 2, 534.
 - ²² Dammer, 2, 592.
 - 23 Rosenheim and Shütte, Zeitsch. anorg. Chem., 24, 238 (1900).
 - ²⁴ Marignac, Jahresber., 1859, p. 108.
 - 25 Richardson and Adams, Amer. Chem. J., 22, 446 (1899).

THE CHEMICAL COMPOUNDS

$$\begin{bmatrix} \operatorname{Sn}_{Br_{2}}^{(BrHAnil.)_{4}} \end{bmatrix} \operatorname{Br}_{2},^{1} \qquad \begin{bmatrix} \operatorname{Sn}_{F_{2}}^{(FNH_{4})_{4}} \end{bmatrix} \operatorname{F}_{2},^{2} \qquad \begin{bmatrix} \operatorname{ONb}_{FH}^{(FK)_{3}} \\ \operatorname{ONb}_{F}^{(FNa)_{3}} \end{bmatrix} \operatorname{F}_{2},^{3}$$

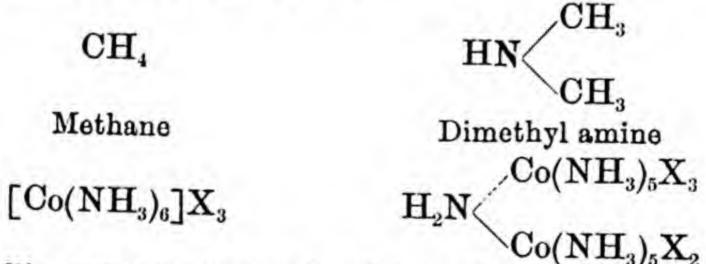
$$\begin{bmatrix} \operatorname{Ta}_{F_{3}}^{(FNa)_{3}} \end{bmatrix} \operatorname{F}_{2},^{4}$$

- ¹ Richardson and Adams, Amer. Chem. J., 22, 446 (1899).
- 2 Ibid.
- ³ Marignac, Ann. Chim. Phys., (4) 8, 34 (1866).
- ⁴ Marignac, ibid., (4) 9, 268 (1866).

6. On Polynuclear Metallic Ammino Complexes.

(a) General.

Polynuclear metallic ammonium compounds differ from the simple ones by having several complexes in one molecule. These complexes are linked together by either single atoms or atomic groups, and neither hydrolysis nor ionization can break these linkings. A metallic atom acts as the central atom of a complex, and the same rules which govern the formation of the simple metallic ammino-complexes are applicable also to the more complicated compounds. Taking the hexammines as representative co-ordination compounds, and methane as a representative valency compound, and placing them side by side, we can look upon polynuclear metallic complexes as being derived from the hexammines in a fashion quite analogous to the linking together of two alkyl residues by another group. Thus:



Simple metallic ammino-compound Complex metallic ammino-compound To be sure, there is an essential difference between the examples; the organic groups are linked to the nitrogen atom by principal valencies, whereas the metallic atoms are linked to the central radicle by auxiliary valencies.

The following are all the groups, as far as is known at present, by which complexes can be linked together: :NH₂, :OH, :O, :O₂, (NO₂), (SO₄). Two metallic atoms can be linked together by one, two, or three such groups; and the groups themselves may be either all the same or all different. Such a group will be termed a

"bridge" (brückenbindung), and it will be seen that dinuclear metallic ammino-complexes can be linked by one, two, or three "bridges." Further, it is possible for a metallic atom to be linked by bridges to one, two, or three other metallic atoms, and by this means the most varied polynuclear metallic ammino-complexes are produced. In the following sections will be found a review of those polynuclear metallic ammino-complexes which have had their constitutions definitely determined. It will be seen that we have here the foundations of quite a new doctrine of the constitution of chemical compounds, from which it is possible to examine the constitution of many classes of inorganic compounds.

(b) Polynuclear Complexes containing one Bridge.

1. Decammine-\u00c4-amino-dicobalti Salts:

This compound has been prepared by the action of liquid ammonia upon dinitrato - octammin - μ - amino - dicobalti nitrate $\left[H_2 N \left[Co_{(NH_3)_4}^{NO_3} \right]_2 \right] (NO_3)_3.$ The salts are coloured from a bluish red to a light red; in aqueous solution they react quite neutral.

$$[(NH_3)_5Cr.OH.Cr(NH_3)_5]X_5^2$$

² J. pr. Chem., (2) 25, 321, 398 (1882); ibid., (2) 45, 279 (1892).

This formula belongs to the rhodo-chromium salts discovered by Jörgensen. They are red in colour, and pass by the action of ammonia into basic salts, which are strongly alkaline and of blue colour. They have the general formula:

$$[(\mathbf{H}_3\mathbf{N})_5\mathbf{Cr} \cdot \mathbf{OH} \cdot \mathbf{Cr}(\mathbf{NH}_3)_5]_{\mathbf{X}_4}^{\mathbf{OH}}$$

These basic salts change easily into the basic erythro-salts, thus * losing water from the μ -ol-group and the free hydroxyl group.

3. Decammine-oxo-dichromi Salts:

$$[(H_3N)_5Cr \cdot O \cdot Cr(NH_3)_5]X_4^3$$

These salts are basic erythro chromium salts, and are quite neutral in aqueous solution. They are isomeric with the rhodo salts when they crystallize with water of crystallization. The oxygen atom is able to take up acids, thus giving rise to compounds resembling oxonium salts.

4. Decammine-hydroxonium-chromi Salts.

$$[(\mathbf{H}_{3}\mathbf{N})_{5}\mathbf{Cr}\cdot\mathbf{O}\cdot\mathbf{Cr}(\mathbf{NH}_{3})_{5}]\mathbf{X}_{4}^{1}$$

$$\dot{\mathbf{H}}$$

$$\mathbf{X}$$

1 Ibid.

This is the constitution of the so-called normal erythro chromium salts, which in aqueous solution react strongly acid. They are consequently isomeric with the normal rhodo salts, into which they are changed by the action of heat:

$$\begin{array}{ccc} \operatorname{Cr}(\operatorname{NH}_3)_5]X_2 & \operatorname{Cr}(\operatorname{NH}_3)_5]X_3 \\ > & > & > & > & > & > & \\ \operatorname{Cr}(\operatorname{NH}_3)_5]X_2 & \rightarrow & & \operatorname{Cr}(\operatorname{NH}_3)_5]X_2 \end{array}$$

Rhodo and erythro salts are consequently valency isomers.

15. Decammine-peroxo-dicobalti Salts:

² Frémy, Annalen, 83, 227, 289 (1852); Gibbs, Proc. Amer. Phil. Soc., 11, 38 (1884); Vortmann, Monatsh., 6, 404 (1885); Werner and Mylius, Zeitsch. anorg. Chem., 16, 245 (1898).

These compounds are the first products of the atmospheric oxidation of cobalt solutions rendered alkaline by ammonia, and they are usually known as oxycobalts. They are brownish-black in colour, and are capable of forming acid salts, e.g. nitrate + HNO₃.

$$[(H_3N)_5C_0 . O_2 . Co(NH_3)_5]X_5$$

3 Ibid.

This class of compounds are called anhydrooxycobaltates. They are formed by the oxidation of the oxycobalts. Their colour is an intensely dark green, and the oxygen molecule in these salts is much more stable than in the oxycobalts.

(c) Polynuclear Complexes containing Two Bridges.

1. Octammine-diol-dicobalti Salts:

$$\left[(\mathbf{H_3N})_4\mathbf{Co}: \mathbf{OH} : \mathbf{Co(NH_3)_4}\right]\mathbf{X_4}^{1}$$

¹ Werner, Ber., 40, 4434 (1907).

These series of compounds are obtained by the dehydration at high temperatures of the hydroxoaquotetrammine cobalti salts:2

$$2\Big[(\mathbf{H}_{3}\mathbf{N})_{4}\mathbf{Co}_{\mathbf{OH}}^{\mathbf{OH}_{2}}\Big]\mathbf{X}_{2} \ \Rightarrow \ \Big[(\mathbf{H}_{3}\mathbf{N})_{4}\mathbf{Co}: \frac{\mathbf{OH}}{\mathbf{OH}}: \mathbf{Co}(\mathbf{NH}_{3})_{4}\Big]\mathbf{X}_{4}$$

The sulphate of the series is produced by the atmospheric oxidation of solutions of cobalt sulphate which had been made alkaline by ammonia.

They are of a magnificent granite-red colour. They differ from the hydroxoaquo salts, with which in some cases they are isomeric, in that they are neutral in solution.

On being treated with concentrated hydrochloric acid they yield cis-dichlorotetrammine cobalti salts (violeo) and cis-diaquotetrammin cobalti salts.³

2. Tetraethylenediamine-diol-dicobalti Salts:
$$\begin{bmatrix} \operatorname{en_2}\operatorname{Co}: \overset{\operatorname{OH}}{\operatorname{OH}}:\operatorname{Co}\operatorname{en_2} \end{bmatrix} X_4^4$$
4 Annalen, 375, 83 (1910).

This series of compounds are prepared by dehydrating the hydroxoaquodiethylenediamine cobalti salts:

$$2\left[\operatorname{en_2}\operatorname{Co}: \operatorname{OH}_2\right]X_2 \rightarrow 2\operatorname{H_2O} + \left[\operatorname{en_2}\operatorname{Co}: \operatorname{OH}_2: \operatorname{Co}\operatorname{en_2}\right]X_2^5$$
5 Werner, loc. cit., p. 272.

They are blood-red salts which react neutral to litmus. Concentrated hydrochloric acid breaks them up into one molecule of cis-diaquodiethylenediamine cobalti chloride and one molecule of cis-dichlorodiethylenediamine cobalti chloride.

² Werner, ibid., p. 4113.

³ Werner, Ber., 40, 4817 (1907).

3. Octammine-μ-amino-ol-dicobalti Salts:

$$\left[(H_3N)_4Co : \frac{NH_2}{OH} : Co(NH_3)_4 \right] X_4^{-1}$$

1 Werner, loc. cit., p. 4065 (1907).

The sulphate of this series of compounds is the chief constituent of Vortmann's sulphate, which is obtained on treating a solution of cobalt nitrate with sulphuric acid; the cobalt nitrate solution previously having been made alkaline with ammonia, and oxidized with atmospheric oxygen.

The salt reacts neutral towards litmus. On being acted on by concentrated acids, e.g. hydrochloric acid, the "ol"-bridge is broken and acidoaquooctammine-μ-amino-dicobalti salts are produced:

$$[(H_3N)_4C_0 \cdot NH_2 \cdot Co_{(NH_3)_4}^X]X_4^2$$

² Werner, Ber., 40, 4605 (1907).

In this way a chloro-, a bromo-, and a nitrato-series can be prepared, and the sulphate in a similar way yields sulphato-octammine-μ-amino-dicobalti salts:

$$\begin{bmatrix} (H_{3}N)_{4}Co \\ H_{2}N & SO_{4} \\ (H_{3}N)_{4}Co \end{bmatrix} X_{3}^{3}$$

² Werner and Baselli, Zeitsch. anorg. Chem., 16, 111 (1898).

The chloride of this last series on heating splits off one molecule of HCl, thus producing the sulphatooctammine- μ -imido-dicobalti salts:

$$\begin{bmatrix} (\mathbf{H}_3\mathbf{N})_4\mathbf{Co} \\ \mathbf{H}\mathbf{N} & \mathbf{SO}_4 \\ (\mathbf{H}_3\mathbf{N})_4\mathbf{Co} \end{bmatrix} \mathbf{X}_2$$

Again, when the chloroaquo-compounds are acted upon by nitrous acid, salts of an octammine- μ -nitro-amino-dicobalti series are produced:

$$\left[(\mathbf{H_3N})_4\mathbf{Co}: \mathbf{\overset{NO_2}{NH_2}}: \mathbf{Co(NH_3)_4}\right]\mathbf{X_4}^2$$

in which the nitro-group is fixed with extraordinary stability, for these salts may be heated with concentrated hydrochloric acid without splitting off the nitro group. 4. Octammine-μ-peroxo-aminocobalte-cobalti Salts:

$$\left[(\mathbf{H}_3\mathbf{N})_4\overset{\mathrm{IV}}{\mathrm{Co}} : \overset{\mathrm{NO}_2}{\mathrm{NH}_2} : \overset{\mathrm{III}}{\mathrm{Co}}(\mathbf{NH}_3)_4\right] \mathbf{X}_4^{-1}$$

Werner, Ber., 40, 67 (1907).

The sulphate of this series is the second constituent of Vortmann's salt; it is of an intense green colour. On reduction with hydriodic acid, salts belonging to the octammine-μ-amino-ol-dicobalti series are produced. On heating the sulphate with concentrated sulphuric acid the oxygen is given off quantitatively in elementary form. We have therefore a method of estimating directly the oxygen in these compounds. Reduction with sulphurous acid transforms these salts into octammine-μ-sulphato-amino-dicobalti salts, and on treating them with nitrous acid octammine-μ-nitro-amino-dicobalti salts result.

5. Diiodo-hexammine-µ-diamino-diplate Salts:

$$\begin{bmatrix}\mathbf{I}_{\mathbf{H}_{3}\mathbf{N})_{3}}\mathbf{Pt} : \mathbf{NH}_{2}}\mathbf{H}_{2} : \mathbf{Pt}_{(\mathbf{NH}_{3})_{3}}^{\mathbf{I}}\end{bmatrix}\mathbf{X_{4}}^{2}$$

² Cleve, Klg. Sv. Vetensk. Akab. Handl., 10, No. 93; Jörgensen, Gmelin-Kraut, 3, 1106.

These salts are produced on splitting off hydriodic acid from the diiodotetrammineplate salts: $[I_2Pt(NH_3)_4]X_2$.

They are salts of a magnificent yellow colour. Two molecules of HX are withdrawn from them by the action of ammonia; the diiodohexammine- μ -diimino-diplate salts resulting:

$$\begin{bmatrix} \mathbf{I}_{\mathbf{1}\mathbf{3}\mathbf{N})_{3}} \mathbf{Pt} : \mathbf{NH} : \mathbf{Pt}_{(\mathbf{NH}_{3})_{3}}^{\mathbf{I}} \end{bmatrix} \mathbf{X}_{2}$$

(d) Polynuclear Complexes containing Three Bridges.

1. Hexammine-μ-amino-diol-dicobalti Salts:

$$\begin{bmatrix} (\mathbf{H}_3\mathbf{N})_3\mathbf{Co} & \mathbf{N}\mathbf{H}_2 \\ \cdot \mathbf{O}\mathbf{H} & \mathbf{Co}(\mathbf{N}\mathbf{H}_3)_3 \end{bmatrix} \mathbf{X}_3^{\ 3}$$

³ Werner, Zeitsch. anorg. Chem., 16, 161 (1898).

The nitrate of this series is obtained by the double decomposition with silver nitrate of melano chloride; the latter being a product of the oxidation of an ammoniacal solution of cobalt chloride. The nitrate acts as the parent substance for the preparation of the other salts. They are brownish-red in colour and neutral towards litmus.

2. Hexammine-\u03c4-amino-peroxo-ol-cobalte-cobalti Salts:

$$\begin{bmatrix} (\mathbf{NH_3})_3\mathbf{Co} \cdot \mathbf{O_2} & \mathbf{Co}(\mathbf{NH_3})_3 \\ \cdot \mathbf{OH} & \cdot \end{bmatrix} \mathbf{X_3}^{1}$$
1 Werner, *ibid*.

One of the compounds derived from the chloride of this series is also to be found in crude melano chloride. Consequently when melano chloride is treated with silver nitrate, the nitrate of the former series and the nitrate of this are produced simultaneously. Just as in the previous case, the other salts of this series are prepared from the nitrate, but they may also be prepared by heating an aqueous solution of the octammine-μ-peroxo-amino-cobalte-cobalti salts with ammonium chloride:

$$\begin{split} & \left[(\mathbf{H}_{3}\mathbf{N})_{4}\overset{III}{Co} : \overset{N}{\mathbf{H}_{2}} : \overset{IV}{Co}(\mathbf{N}\mathbf{H}_{3})_{4} \right] X_{4} + \mathbf{H}_{2}\mathbf{O} \\ = & \left[(\mathbf{H}_{3}\mathbf{N})_{3}\overset{III}{Co} : \overset{N}{\mathbf{H}_{2}} : \overset{IV}{\mathbf{Co}}(\mathbf{N}\mathbf{H}_{3})_{3} \right] X_{3} + \mathbf{X}\mathbf{H} + 2\mathbf{N}\mathbf{H}_{3} \\ & \cdot \overset{O}{\mathbf{O}}\mathbf{H} : \overset{O}{\mathbf{O}}\mathbf{H} : & \overset{O}{\mathbf{O}}\mathbf{H}^{2} : \overset{IV}{\mathbf{O}}(\mathbf{N}\mathbf{H}_{3})_{3} \end{split}$$

These salts are of an intense green colour, and form solutions which are neutral towards litmus.

3. Hexammin-triol-dicobalti Salts:
$$\begin{bmatrix} \cdot & OH \\ (H_3N)_3Co & OH \\ \cdot & OH \end{bmatrix} Co(NH_3)_3 X_3^2$$

² Werner, Ber., 40, 4834 (1907).

The members of this series are produced under various conditions from triammin cobalt salts. The following is a general equation illustrating their formation:

$$2[(\mathbf{H}_{3}\mathbf{N})_{3}\mathbf{Co}(\mathbf{OH}_{2})_{3}]X_{2} = \begin{bmatrix} (\mathbf{H}_{3}\mathbf{N})_{3}\mathbf{Co} & \mathbf{OH} \\ (\mathbf{H}_{3}\mathbf{N})_{3}\mathbf{Co} & \mathbf{OH} \\ \mathbf{OH} & \mathbf{Co}(\mathbf{NH}_{3})_{3} \end{bmatrix} X_{3} + 3\mathbf{H}_{2}\mathbf{O} + 3\mathbf{H}\mathbf{X}$$

They are brownish-red salts which yield solutions neutral to litmus, and which crystallize particularly well. Concentrated acids break one of the "ol" bridges, thus producing acidoaquohexammindioldicobalti salts:

$$\begin{bmatrix} (\mathbf{H_3N})_3 & \cdot & \mathbf{OH} & \cdot & (\mathbf{NH_3})_3 \\ \mathbf{X} & \cdot & \mathbf{OH} & \cdot & \mathbf{OH_2} \end{bmatrix} \mathbf{X_3}$$

In this way an acetoaquo-series is produced. Using nitrous acid a nitratoaquo series is obtained which, on treating with liquid ammonia, takes up two molecules of ammonia, thereby being transformed into the octammine-diol-dicobalti series:

$$\begin{bmatrix} O_{3}N & OH & OH_{2} \\ Co & Co \\ (H_{3}N)_{3} & OH & (NH_{3})_{3} \end{bmatrix} (NO_{3})_{3} + 2NH_{3}$$

$$= \begin{bmatrix} (H_{3}N)_{4}Co & OH & Co(NH_{3})_{4} \\ OH & OH & Co(NH_{3})_{4} \end{bmatrix} (NO_{3})_{4} + 2H_{2}O^{-1}$$

¹ Annalen, 375, 121 (1910).

The triol salts are decomposed by concentrated hydrochloric acid, one of the products being trichlorotriammine cobalt, and another a chloro salt of triaquotriammine cobalti chloride, which latter compound is one of the primary decomposition products:

$$\begin{bmatrix} (\mathbf{H}_{3}\mathbf{N})_{3}\mathbf{Co} & .\mathbf{OH} & .\mathbf{Co}(\mathbf{NH}_{3})_{3} \\ .\mathbf{OH} & .\mathbf{Co}(\mathbf{NH}_{3})_{3} \end{bmatrix} \mathbf{Cl}_{3} + 3\mathbf{HCl} = (\mathbf{H}_{3}\mathbf{N})_{3}\mathbf{Co}\mathbf{Cl}_{3} \\ + [(\mathbf{H}_{2}\mathbf{O})_{3}\mathbf{Co}(\mathbf{NH}_{3})_{3}]\mathbf{Cl}_{3}$$
² Werner, Ber., 39, 2674 (1906).

when the triol salts are treated with nitrous acid hexammine- μ nitro-diol-dicobalti salts are produced.

$$\begin{split} & \begin{bmatrix} (\mathbf{H}_{3}\mathbf{N})_{3}\mathbf{Co} \cdot \overset{OH}{OH} \cdot & \mathbf{Co}(\mathbf{NH}_{3})_{3} \end{bmatrix} \mathbf{X}_{3} + \mathbf{HNO}_{2} \\ & \cdot O\mathbf{H} \cdot & \mathbf{Co}(\mathbf{NH}_{3})_{3} \end{bmatrix} \mathbf{X}_{3} + \mathbf{HNO}_{2} \\ = & \begin{bmatrix} (\mathbf{H}_{3}\mathbf{N})_{3}\mathbf{Co} \cdot \overset{NO}{OH} \cdot & \mathbf{Co}(\mathbf{NH}_{3})_{3} \\ & \cdot O\mathbf{H} \cdot & \mathbf{Co}(\mathbf{NH}_{3})_{3} \end{bmatrix} \mathbf{X}_{3} + \mathbf{H}_{2}\mathbf{O}^{-1} \end{split}$$

The nitro-group is held exceedingly firmly on these salts, for on boiling with hydrochloric and hydrobromic acids a second ol-bridge is broken and dichloro- or dibromo-hexammine- μ -nitro-ol-dicobalti salts are produced:

$$\begin{bmatrix} \operatorname{Cl} & \cdot \operatorname{NO}_2 & \operatorname{Cl} \\ \operatorname{Co} & \operatorname{Co} \\ (\operatorname{H}_3\operatorname{N})_3 & \cdot \operatorname{OH} & \cdot & (\operatorname{HN}_3)_3 \end{bmatrix} X_2 \text{ and } \begin{bmatrix} \operatorname{Br} & \cdot \operatorname{NO}_2 & \operatorname{Br} \\ \operatorname{Co} & \operatorname{Co} \\ (\operatorname{H}_3\operatorname{N})_3 & \cdot \operatorname{OH} & \cdot & (\operatorname{NH}_3)_3 \end{bmatrix} X_2$$

(e) Polynuclear Complexes containing Four Bridges. Tetraethylenediamine-tetrol-cobalto-dicobalti compounds:

$$[(H_2O)_2Co(OH)_4(Co\ en_2)_2]X_4^3$$

3 Werner, *ibid.*, **40**, 4426 (1907).

The sulphate of this series is precipitated in the form of fine, long, pink needles when a solution of cobalt sulphate, to which ethylendiamine has been added, is oxidized by atmospheric oxygen. Salts belonging to this series are also formed when other cobalt salts are oxidized under like conditions. Both concentrated hydrochloric acid and hydrobromic acid decompose these complexes into cobalto salts and cis-diaquodiethylenediamine cobalti salts, $[(H_2O)_2Coen_2]X_3$.

- (f) Polynuclear Complexes containing Six Bridges.
- 1. Dodecammine-hexol-tetracobalti Salts:

 $[Co(OH_3)_6[Co(NH_3)_4)]_3]X_6.^2$

Salts belonging to this series are produced from the most diverse tetrammine cobalti salts, and their colour varies from brown to pitch black. The sulphate and the thionate are insoluble in water, but are all decomposed by concentrated hydrochloric acid into diaquotetrammine cobalti salts. Finally, it is noteworthy that these salts are polymeric with the hexamminetrioldicobalti salts.

2. Hexaethylenediamine-hexol-tetracobalti Salts:

[Co(OH)6(Co en2)3]X6.2

The nitrate is easiest prepared. It crystallizes, after standing a short time, in long, dark brown needles from a solution of cobalt nitrate, which has been oxidized by atmospheric oxygen, and to which ethylene diamine has been added. The other salts may be prepared by double decomposition from the nitrate. They are all easily soluble in water. Their solutions are yellowish-brown and neutral to litmus. Concentrated hydrochloric and hydrobromic acids decompose the salts, producing good yields of cis-diaquodiethylene cobalti salts: $[(H_2O)_2Co\ en_2]X_3$.

(g) Polynuclear Complexes of Unknown Constitution.

As well as all these polynuclear complexes which have had their constitutions cleared up, there exist a great number of others to which it has not as yet been possible to give constitutions. To

² Werner, ibid., p. 2103.

Werner, Ber., 40, 4426 (1907).

this class belong the fuskocobaltates of Frémy,¹ the rhodoso-chromates of Jörgensen,² and the ethylenediaminerhodosochromates of Pfeiffer.³ Lastly, there exist very many polynuclear cobalt complexes which I have come across during my years of work on these compounds, and which have not yet received a thorough examination.

7. On Co-ordinatively Unsaturated Substitution Compounds.

(a) Behaviour and Constitution.

When a compound of the formula MeX₂ takes up four molecules of ammonia or of amine, both X radicles in the resulting compound X₂Me(NH₃)₄ should remain directly attached to the metallic atom, i.e. the addition-compound which has thus been formed should have the constitution:

$$H_3N$$
 H_3N
 $Me < X$
 H_3N

An example of this type is to be found in tetrahydroxylamineplatohydrate

$$(NH_2OH)_4Pt < OH$$

This compound, in opposition to all true hydroxides of the metallic ammino-complexes—which are strong bases, absorb carbon dioxide from the air, and dissolve easily in water, etc.—is insoluble in water and exhibits no alkaline character. Hydrochloric acid, however, converts it into a chloride, (HO. H₂N)₄PtCl₂, which behaves just as if it had been derived from a true metallic ammino-base. It displays none of the properties which characterize chlorine when directly bound to platinum, viz. it is not yellow but colourless, it does not dissolve in water with difficulty but with great ease, silver nitrate does react with its aqueous solution precipitating all the chlorine, and, finally, the addition of alkali to this solution precipitates the free base. It follows, therefore, from these properties that the chlorine is attached indirectly to the central atom. As a

¹ Frémy, Ann. Chim., (3) 35, 257 (1852).

² Jörgensen, J. pr. Chem., 45, 260, 270 (1892).

³ Pfeiffer, Zeitsch. anorg. Chem., 29, 128 (1902).

result of this ionogene binding the chlorine atoms are very mobile, and are therefore able to seek out for themselves more favourable positions in the molecule, and thus bring about a change in the constitution of the molecule. As a matter of fact, tetrahydroxylamineplato chloride behaves as if it had the following constitution:

This behaviour of tetrahydroxylamineplato chloride shows that substitution compounds can be formed before all the co-ordination positions are occupied. It is impossible to predict at which phase in the formation of the complex the acid residues will become indirectly bound, thus bringing about a change in the constitution. It may possibly take place on the addition of the first molecule, thus:

$$MeX_2 + NH_3 = Me$$
 X
 $NH_3)X$
 X

In other cases it takes place after the addition of two, three, or more molecules.

This behaviour is different in different compounds, and is dependent upon the nature of the central atom and of the acid residues which are being taken up. Obviously, then, it is necessary to examine each individual case in order to determine at what point of the addition the acid residues first receive ionogene properties.

The examination of the metallic ammonium salts has shown that this transformation takes place in the divalent salts very early in their formation, for both acid residues have ionic properties even after the addition of four molecules of ammonia. This is true of the following compounds:

[Pt(NH₃)₄]X₂,¹ [Cu(NH₃)₄]X₂,² [Ni(NH₃)₄]X₂,³ [Pd(NH₃)₄]X₂.⁴

- ¹ Reiset, Compt. rend., 11, 711; 18, 1100; Ann. Chim., (3) 11, 417 (1844).
- ² Kane, Ann. Chim., 72, 273 (1809).
- ³ Dammer, 3, 511.
- ' Deville and Debray, Compt. rend., 86, 926 (1878).

The change of the acid residues from the non-ionogene linking into the ionogene linking may be followed very prettily in the salts of divalent platinum, as the following shows.

In the platodiammine salts, corresponding to the formula [Pt(NH3)4]X2, both acid residues are attached to the platinum by ionogene linkings. This is proved by the precipitation of the acid residues, by the electrical conductivity, etc. Through loss of one molecule of ammonia platomonodiammine salts, $Pt(NH_3)_3X_2$, are produced. The chloride of this series has the formula $Pt(NH_3)_3Cl_2$, and only one chlorine has ionogene properties, for in solution the one has all the properties of chloridion and the other has none of them. Accordingly the compound has been given the following constitutional formula:

¹ Peyrone, Annalen, 51, 1; 55, 205; 61, 178 (1847).

in which one chlorine is directly attached to platinum and the other indirectly.

When the platodiammine salts lose two, or the platomonodiamine salts one molecule of ammonia, compounds with the formula $Pt(NH_3)_2X_2$ are produced. In these compounds both acid residues must be directly attached to the platinum atom, since both have but little capacity for reaction.

Two compounds with the formula Pt(NH₃)₂Cl₂¹ are known, in which both chlorine atoms are indirectly attached to the central atom. The meaning of this will be discussed later.

The changing behaviour of the acid residues in these compounds may be followed experimentally by their reactions with potassium platinous chloride:

- 1. $[Pt(NH_3)_4]Cl_2 + K_2PtCl_4 = [Pt(NH_3)_4][PtCl_4] + 2KCl^4$
- 2. $2\left[Pt_{(NH_3)_3}^{Cl}\right]Cl + K_2PtCl_4^2 = \left[Pt_{(NH_3)_3}^{Cl}\right]_2\left[PtCl_4\right] + 2KCl^3$
- 3. $\left[\operatorname{Pt}^{\operatorname{Cl}_2}_{(\operatorname{NH}_3)_2}\right] + \operatorname{K_2PtCl_4}^4$ no reaction.
 - ¹ Magnus, Pogg. Ann., 14, 242 (1828).
- ² Cleve, On Ammoniacal Platinum Bases (Stockholm, 1872); Werner and Herty, Zeitsch. physikal. Chem., 38, 331 (1901).
 - ³ Peyrone, annalen, 51, 1 (1844).
 - 4 Werner and Miolati, Zeitsch. physikal. Chem., 12, 35; 14, 506 (1894).

It may be noted also that tetrahydroxylamine platochloride displays a behaviour analogous to that of the ammonium compounds, i.e. the loss of molecules of hydroxylamine causes both chlorine atoms to lose their ionogene properties.

¹ Cleve, On Ammoniacal Platinum Bases. Stockholm, 1872.

From the behaviour of the compounds Me(NH₃)₄X₂ and those poorer in ammonia, it is clear that the complex [Me(NH3)4], in spite of it being co-ordinatively unsaturated, plays the same rôle as is played by the saturated radicle [Me(NH₃)₆]. Since in the compounds [Me(NH3)4]X2 all the acid residues have ionic properties and lose them when ammonia leaves the complex, it follows that we have here a new type of complex radicle to be placed beside the type [Me(NH₃)₆]. In the latter, however, all the co-ordination positions are occupied, but in the former this is not the case, for in some cases it is possible for the central atom to take up further molecular components. For example, Cleve showed the compound $Pt\begin{bmatrix}(NH_3)_2\\(NH_2,C_6H_5)_2\end{bmatrix}SO_4$, which corresponds to tetrammineplato chlorine, could take another molecule of aniline, and I have shown that well-defined copper compounds with the formula: (Cu en₃)X₂¹ can be prepared. But these new compounds are usually rather unstable, and decompose very easily into the original compounds. This is true both of Cleve's compound, which easily loses a molecule of aniline, and of the triethylenediamine copper salts, which in aqueous solution give up a molecule of ethylene diamine.

From these and similar facts it is to be concluded that the transition of the acid residue from non-ionogene into ionogene linking is connected with the degree of saturation of the central atom, for the central atom is almost saturated when these changes take place. That the central atom is almost completely saturated when four radicles are directly bound to it is to be seen in the fact that such central atoms form the complex MeR, with other classes of radicles. Thus divalent platinum forms the following salts:

¹ Thomsen, J. pr. Chem., (2) 15, 1295 (1877).

Dammer, Hand. anorg. Chem., 3, 835.
 Lang, J. pr. Chem., 83, 415 (1861).

⁵ Birnbaum, Annalen, 139, 164 (1866); 152, 137 (1869); 159, 116 (1871).
⁶ Ibid.

¹ Lang, loc. cit.

⁸ Nilson, Ber., 10, 930 (1877); 11, 879 (1878).

Dammer, loc. cit., p. 841.

Werner, Zeitsch. anorg. Chem., 21, 201 (1899).

and nickel and palladium form similarly constituted double salts:

 $\begin{array}{lll} [NiCy_4]R_{2},^1 & [NiF_4]R_{2},^2 & [Pd(NO_2)_4]R_{2},^3 & [PdCy_4]R_{2},^4 & [Pd(SCN)_4]R_{2},^5 \\ & [PdCl_4]R_{2},^6 \end{array}$

¹ Dammer, loc. cit., p. 517. ² Ibid., p. 505.

3 Ibid., p. 886 (cf. Zeitsch. analyt. Chem., 5, 403).

⁴ Ibid., pp. 891 and 892. ⁵ Ibid.

6 Rössler, Zeitsch. anorg. Chem., 1866, p. 175.

Great support is given to these ideas by the fact that similar phenomena are to be found in a group of compounds the constitutions of which are beyond doubt, viz. the oxygen acids of the metalloids. It is well known that different metalloids are characterized by their acids and salts, *i.e.* those richest in oxygen, containing the complex radicle MO₄; this may be seen in the following examples: R₃PO₄, R₃AsO₄, R₂SO₄, R₂SeO₄, RClO₄, etc.

Now, these compounds and those metallic ammino-complexes which contain the radicle $Me(NH_3)_4$ are very similar in their behaviour. For just as the loss of a molecule of ammonia by the compound $[Me(NH_3)_4]X_2$ causes an acid residue to pass from the ionic into the non-ionic condition, so does the loss of an atom of oxygen by the molecule $[MO_4]H_m$ cause a hydrogen atom to pass from the ionic into the non-ionic condition.

Examples of this analogy are to be found in the following constitution formulæ:

$$\begin{bmatrix} H_3N & NH_3 \\ H_3N & NH_3 \end{bmatrix} X_2 \qquad \begin{bmatrix} H_3N & NH_3 \\ H_3N & X \end{bmatrix} X \qquad \begin{matrix} H_3N & X \\ H_3N & X \end{matrix}$$
Platosammine salts
Platosammine and Platosemidiammine salts

$$\begin{bmatrix} O : P & O \\ O & P & D \end{bmatrix} H_3 \qquad \begin{bmatrix} O : P & O \\ O & P & H \end{bmatrix} H_2 \qquad \begin{bmatrix} O : P & H \\ O & P & H \end{bmatrix} H \qquad \begin{array}{c} O : P & R \\ R & P & R \end{array}$$
Phosphoric acid Phosphorous acid Hypophosphorous acid oxide

Similar phenomena are exhibited by the oxygen acids of sulphur:

$$\begin{bmatrix} O:SO\\O:SO\end{bmatrix}H_2 & \begin{bmatrix} O:.O\\O:S.H\end{bmatrix}H & O:.R\\O:S.R \\ Sulphuric acid & Sulphurous acid & Sulphinic acid \\ \end{bmatrix}$$

However, the great mobility of the hydrogen in those acids which contain less than four atoms of oxygen:

$$\mathbf{H}_{2}\begin{bmatrix}
\mathbf{O} \\
\mathbf{OPH} \\
\mathbf{O}
\end{bmatrix}$$
 and $\mathbf{H}\begin{bmatrix}
\mathbf{O} \\
\mathbf{OS} \\
\mathbf{H}\end{bmatrix}$

renders tautomeric phenomena possible, so that under some conditions it is possible to obtain derivatives with the following formulæ:

$$R_3 \begin{bmatrix} O \\ OP \\ O \end{bmatrix}$$
 and $R_2 \begin{bmatrix} O \\ OS \\ O \end{bmatrix}$

and it is quite possible for similar tautomeric phenomena to be observed in the metallic ammino-complexes. Thus it is to be expected that the compounds [Me(NH₃)₃]X₂, according to the nature of the acid residue, may have either of the following constitutional formulæ:

$$X\begin{bmatrix} H_3N & X \\ H_3N & Pt & X \\ H_3N & NH_3 \end{bmatrix}$$
 or $X_2\begin{bmatrix} H_3N & Me \\ H_3N & NH_3 \end{bmatrix}$

We can extend consequently the statement made in the introduction on p. 179, viz. the acid residue passes into indirect attachment in different salts, when different numbers of ammonia molecules have been added, by saying that the constitution of the different salts of the same complex radicle varies with the nature of the acid residue. Hence it is to be expected that two salts of the same metal, say the chloride and nitrate, can behave in different ways, so that the addition products with two molecules of ammonia correspond to the formulæ:

In conclusion, it may be noted that by substituting ammonia by water, halide, etc., it is possible to prepare many different types of analogously constituted, co-ordinatively unsaturated compounds. To this class belongs the blue potassium copper chloride, CuCl₂ + 2KCl + 2H₂O, which probably has the following formula, [(KCl)₂Cu(OH₂)₂]Cl₂, and many others to which, as yet, definite constitutions have not been given.

Between the chloride and the bromide of (Cu en) a similar difference appears to exist. The chloride is blue, like the ammonium compounds, while the bromide is intensely green.

(b) Transition Series between Co-ordinatively Unsaturated Metallic Ammino Complexes and Complex Salts.

We have seen that substitution- and addition-compounds are related to one another in such a way as to make it possible to prepare a complete transition series, as, for example, that existing between the metallic ammino-compounds and the complex salts. This is also true of co-ordinatively unsaturated addition compounds.

Such a transition series is known for the salts of divalent platinum. As an illustration of this the transition series of chlorine compounds may be given:

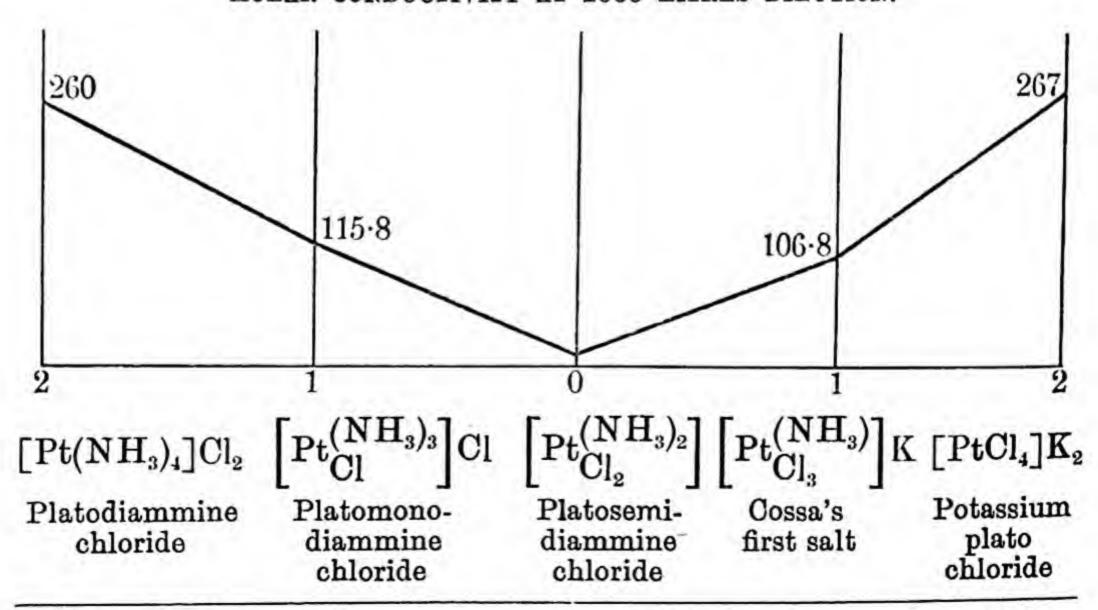
- ¹ Reiset, Compt. rend., 11, 711; 18, 1100; Ann. Chim. Phys., (3) 11, 417 (1844).
 - ² Cleve, On Ammoniacal Platinum Bases, p. 158. Stockholm, 1872.
- ³ Dammer, Handb. anorg. Chem., 3, 815; Werner and Miolati, Zeitsch. physikal. Chem., 12, 35; 14, 506 (1894).
 - 4 Cossa, Ber., 23, 2503 (1890).
 - ⁵ Dammer, loc. cit., p. 798.

Since both the latter compounds are broken up in aqueous solution into the following ions:

$$\begin{bmatrix} PtNH_3 \\ Cl_3 \end{bmatrix}$$
 and \ddot{K} ; $[PtCl_4]$ and $2K$ +

the conductivity curve is as follows:1

MOLAR CONDUCTIVITY AT 1000 LITRES DILUTION.



Werner and Miolati, loc. cit.; Werner and Hertz, ibid., 38, 331 (1901).

A very pretty transition series of this description has been prepared by Kohlschütter 1 from the thiocarbamide compounds of monovalent copper.

$$\begin{bmatrix} Cu(Thi.)_3 \end{bmatrix} Cl, \quad \begin{bmatrix} Cu_{(Thi.)_2}^{Cl} \end{bmatrix}, \quad \begin{bmatrix} Cu_{Thi.}^{Cl_2} \end{bmatrix} H, \quad \begin{bmatrix} CuCl_3 \end{bmatrix} H_2$$

8. The Co-ordination Complexes formed from Compounds of Hydrogen.

- (a) The Oxonium Salts.
- 1. The Constitution of Oxonium Salts.

It has been seen already that many compounds possess the property of being able to form addition compounds with water and its substitution products, and from this it was concluded that the central atom possessed an auxiliary valency.

Examples of this type are:

$$Cl_3Au \cdot OH_2$$
, $Cl_4Pt : {OH_2 \atop OH_2}$, $[Ni(OH_2)_6]X_2$, $[Cr(OH_2)_6]Cl_3$, $[Cr(OH_2)_4]Cl_3$

Since the capacity to form such addition compounds is a general property, and since there hardly exists an electropositive element which does not possess it, then hydrogen would occupy an exceptional position if it did not also possess this capacity in its salts, i.e. the acids. It is to be expected, in consequence of this, that the hydrogen of acids will display a capacity for the addition of compounds resembling oxides. This expectation is fulfilled, and the nature of this type of compound is illustrated by the following examples. Acids yield hydrates, thus nitric acid yields the following:

$$NO_3H \cdot OH_2$$
 and $NO_3H \cdot 3OH_2^2$
m.p. -38° m.p. -18.5°

and perchloric acid the following:3

¹ Ber., 36, 1151 (1903).

Küster and Kreeman, Zeitsch. anorg. Chem., 41, 1 (1904).
 Van Wyk, ibid., 48, 1 (1905).

Such hydrates are often represented as high basic acids without confirming this representation by preparing the corresponding salt or ester.

Such a method of representing these hydrates appears to be all the more improbable when the fact is remembered that not only oxygen acids, as nitric acid, but also the halogen acids form hydrates, e.g.:

$$HCl + 2H_2O$$
, $HCl + 3H_2O$, $^1HBr + 2H_2O$, $HBr + 3H_2O$, $HBr + 4H_2O$, $^2HI + 2H_2O$, $HI + 3H_2O$, and $HI + 4H_2O$.

- ¹ Pikering, Ber., 26, 277 (1893).
- ² Pikering, Phil. Mag., (5) 36, 111 (1893).
- ³ Pikering, Ber., 26, 2307 (1893).

When it is remembered that the acids form similar addition products with organic derivatives of water, as, for example, with alcohols, ethers, aldehydes, ketones, etc., some of which, at any rate, cannot be formulated as derivatives of higher basic acids, as, for example, the following compounds:

$$H_3C$$
 O. HCl H_3C O. HBr H_3C O. HI

then it appears probable, that all such addition products of the oxygen compounds should be formulated differently.

Following the example of Collie and Tickle¹ and of Baeyer and Villiger,² attempts have been made to explain the formation of such addition products with organic compounds by supposing oxygen to be tetravalent. The same hypothesis had been used earlier to explain the addition of dimethyl ether to hydrochloric acid. The general name of oxonium salts has been applied to these compounds. According to this conception the addition product formed by the addition of dimethyl ether to hydrochloric acid is to be formulated

Oxonium formulæ have also been proposed for the products of the addition of organic oxides to metallic salts, while the hydrates, strange to say, have been left untouched.

¹ Trans., 75, 710 (1899).

² Ber., 34, 2679, 3612 (1901).

The theory of tetravalent oxygen makes it possible to bring into agreement the formulæ of many of these addition-compounds, yet it is unable to provide constitution formulæ for all the members of this class. For it excludes all those compounds which contain more oxide molecules than acid residues, *i.e.* all such compounds as

$$MeX_2 + 3R_2O$$
, $MeX_2 + 4R_2O$, $MeX_2 + 6R_2O$, etc.

The formulæ, however, embrace many hydrates and compounds similar to hydrates, which on account of their mode of formation and properties are quite comparable to the oxonium salts. We must, therefore, choose a theory which will provide a constitution for the oxonium salts and also a satisfactory constitution for all those compounds which are formed by a similar addition of oxides. Such a foundation is to be obtained from our discussion of the constitution of the hydrates, when it was supposed that oxygen not only possesses two principal valencies but also an auxiliary valency, the saturation of which leads to the formation of addition-compounds:

$$\begin{array}{c}
R \\
R
\end{array} O + MeX = \begin{array}{c}
R \\
R
\end{array} O \dots MeX$$

When, in this equation, Me is replaced by H, an equation accounting for the formation of the addition-compounds of oxides with acids is obtained. The constitution of the oxonium salts, therefore, will be represented by formula II.; the old formula which contains tetravalent oxygen is also given for comparison:

Consequently, according to our ideas oxonium salts do not contain tetravalent oxygen, but, in a purely structural chemical sense, trivalent, i.e. oxygen links together three radicles.

The existence of anomalous oxonium salts gives support to the auxiliary valency formula of oxonium salts. The existence of anomalous oxonium salts is not easily explained by tetravalent oxygen, for if the addition-compounds of oxides with acids be

explained by this theory, then the oxygen atom in $O \subset_{\mathbf{R}}^{\mathbf{R}}$ should be saturated when a single molecule of HX has been taken up:

A further addition of $O \subset_{R}^{R}$, is impossible, or it must be supposed

that oxygen chains are formed in the following way:

But no satisfactory reasons in favour of such a formula can be obtained, and it is all the more untenable since chain-formulæ for the hydrates of metallic salts, for the metallic ammino-complexes, etc., to-day are accepted universally as incorrect.

On the other hand, the auxiliary valency formula leads us to expect that the hydrogen in HX, just as metallic atoms, would be able to exercise more than one auxiliary valency, and on this account would take up more than one molecule of the oxygen compound—a behaviour which finds expression in the following formulæ:

$$X.H.OR_2$$
, $X.H$ OR_2 OR_2 OR_2 OR_2 OR_2 etc.

Compounds in which hydrogen takes up more than one molecule of oxide we will call "anomalous oxonium salts." A great number of these are already known, thus pyrone forms a chloroplateate with chloroplatinic acid, which has the composition $[PtCl_6]H_2$ $(C_5H_4O_2)_4$, and consequently must have the following constitution:

$$[PtCl_6] \begin{cases} H_{\bullet}OC_{\flat}H_{\bullet}O \\ OC_{\flat}H_{\bullet}O \\ OC_{\flat}H_{\bullet}O \end{cases}$$

Bain has prepared from dimethylethylpyrone the anomalous chlorhydrate $(C_9H_{12}O_2)_2HCl + 2H_2O$.

Further, the following perhalide salts are known:

 $(C_7H_8O_2)_2HBr_3$, $(C_7H_8O_2)_2HI_3^{-1}$ Dimethylpyrone, $(CH_3COOH)_2HBr_3$, $(C_{17}H_4O)_2HI_5$ Dibenzylacetone, $(C_{11}H_{12}O_2)_2HI_5$ Monoanisylacetone, $(C_{19}H_{18}O_3)_2HI_5$ Dianisylacetone, and $(C_{19}H_{18}O_3)_2HI_3$.

¹ Collie and Tickle, loc. cit., 77, 1115 (1900).

² Steiner, Ber., 7, 184 (1874).

³ Hantzsch, Annalen, 349, 1 (1906).

The hypobromperbromide of santonine of Wedekind is to be formulated thus:

Pickard and Kenyon have prepared a great many anomalous oxonium salts which are derivatives of phosphine oxide corresponding to the following general formulæ:

$$2R_3PO . HAuCl_4$$
 $2R_3PO . HHgI_3$ $4R_3PO . H_2PtCl_6$ $6R_3PO . H_2PtCl_6$

Borsche and Menz² have observed an anomalous chloroauriate of phenyl-R-pentenon. I³ have also drawn attention to some inorganic anomalous oxonium salts. For, starting with the hydro-oxonitrotetrammine cobalt salts and acting on them with ammonium salts, it was possible to prepare the following compounds, which crystallize magnificently:

$$\begin{split} & \left[\text{Cl} \binom{\text{O}_2 \text{N}}{(\text{H}_3 \text{N})_4} \text{CoOH} \right] \right]_2 \text{HCl} + 4 \text{H}_2 \text{O} \\ & \left[\text{Br} \binom{\text{O}_2 \text{N}}{(\text{H}_3 \text{N})_4} \text{CoOH} \right] \right]_2 \text{HBr} + 4 \text{H}_2 \text{O} \quad \left[\text{I} \binom{\text{O}_2 \text{N}}{(\text{H}_3 \text{N})_4} \text{CoOH} \right] \right]_3 \text{HI} \end{split}$$

A further ground for the acceptation of the auxiliary valency formula is found in the fact that constitutional formulæ concordant with their formation and properties are given to the analogous addition products of metals and acids.

Just as the hydrogen of acids is able to form addition compounds, so in like manner the metallic atoms in certain salts take up oxygen compounds. Copper chloride in aqueous solution combines with

¹ Trans., 89, 262 (1906).

² Ber., 41, 197 (1908).

³ Ibid., 40, 4122 (1907).

dimethyl pyrone, forming a compound with the formula Cl_2Cu . $\text{C}_7\text{H}_8\text{O}_2$, and the constitution of which corresponds to the ordinary salts of dimethyl pyrone, thus:

$$OC_7H_8O + HCl = OC_7H_8O \dots HCl$$

 $OC_7H_8O + CuCl_2 = OC_7H_8O \dots CuCl_2$

Cobalt chloride, zinc chloride, mercuric chloride, etc., form similar addition compounds.

Xanthone and other oxygen compounds also yield such addition-compounds. Kehrmann prepared the nitrate of phenanthrene quinone, and this latter compound gives well-characterized addition products with zinc chloride, mercuric chloride, and mercury cyanide. Pickard and Kenyon¹ have prepared the following anomalous oxonium salts of phosphine oxide:

$$2(CH_3)_3Po.ZnI_2$$
, $2(C_2H_5)_3PO.CuCl_2$, $2(C_6H_5)_3PO.CdI_2$, $2(C_6H_5)_3PO.ZnCl_2$, $2(C_6H_5)_3PO.HgCl_2$, $2(C_6H_5)_3PO.CoCl_2$, $2(C_6H_5)_3PO.ZnI_2$

and the following two were already known:

$$2(C_2H_5)_3PO \cdot ZnI_2^2$$
 $2(C_2H_5)_3PO \cdot CuSO_4^3$

Borsche and Menz have shown that phenyl-R-pentenone forms crystallized addition-products with mercuric chloride and ferric chloride.

From all these facts it must be concluded that since organic oxygen compounds are able to form addition-compounds with both acids and metallic salts, similar constitutional formulæ must be given to the resulting products of both classes.

2. Review of Oxonium Salts.

(a) The Inorganic Oxonium Salts.

All inorganic compounds which are similar to hydrates and have the general formula,

(R being an inorganic radicle), are to be considered as inorganic oxonium salts.

¹ Trans., 89, 262 (1906).

² Hofmann, Annalen, Suppl. 1861, p. 2.

³ Pebal, Annalen, 120, 194 (1862).

⁴ Ber., 41, 197 (1908).

The hydrates of the acids $(H_2O)_2$ HCl, $(H_2O)_2$ HBr, etc., form one small group. But much more numerous are those oxonium salts in which the hydrogen of the acid is linked to the oxygen of a metallic hydroxide, and consequently has the following formula:

$$\begin{bmatrix} \mathbf{Me} & \mathbf{O} & \mathbf{H} \end{bmatrix} \mathbf{X}$$

With the metallic atom other groups, such as ammonia, water, etc., may be bound, so that the corresponding formula then is:

$$\begin{bmatrix} \mathbf{A_n Me} \\ \mathbf{H} \end{bmatrix} \mathbf{O} \cdot \mathbf{H} \mathbf{X}$$

These compounds, which are of considerable theoretical importance, have received much attention during the last few years, and the results have shown that all hydrated metallic salts, in which the acid residue is indirectly linked to the central atom, belong to this group of oxonium salts. In aqueous solution many of these salts decompose according to the equation:

$$\begin{bmatrix} A_n Me \\ H \end{bmatrix} O - H X \rightleftharpoons A_n Me \\ H > O + HX$$

i.e. they are partly hydrolytically dissociated, and therefore the solution is acid. Bases regenerate the original oxide:

from which, by the action of acids, the oxonium salts (aquo salts) may be obtained again. The property of forming oxonium salts is one which belongs to the metallic hydroxides in general, and will be more fully discussed when treating of the theory of bases.

(b) The Organic Oxonium Salts.

To the organic oxonium salts belong not only pyrone-like compounds, as Collie and Tickle assumed, but also, as Baeyer and Villiger pointed out, all the addition-compounds of acids to alcohols, ethers, aldehydes, ketones, etc. The simplest organic oxonium salts are those which have been prepared lately by McIntosh, namely:

¹ Ber., 84, 2679 (1901).

² J. Amer. Chem. Soc., 27, 26, 1013 (1905).

CH₃OH . HBr (m.p. -14°), CH₃OH . HI (m.p. -48°), C₂H₅OH . HNO₃ (m.p. -30°), (CH₃)₂O . HBr (m.p. -22°), (CH₃)₂O . HI (m.p. -15°), (CH₃)₂CO . HNO₃ (m.p. -18°), [(C₂H₅)₂O]₂ . HOSO₂Cl (m.p. -45°). [(CH₃)₂CO]₂HOSO₂Cl (m.p. -30°).

The following compounds also must be considered as oxonium salts: the nitrate of cinnamic aldehyde, the iodohydrate of camphor, the chlorhydrate of orcinphthaleine, the sulphate of fluoresceine, the acid compounds of aurine, the chlorhydrate of dibenzoylacetone, the halide acid compounds of cineol, the salts of dimethylpyrone, and all the compounds of ferro-, ferri-, cobalticyanic acids, and phosphorous tungstic acid with alkylene oxides, alcohols, esters, aldehydes and ketones which Baeyer and Villiger have prepared.

The salts of the natural dyes which A. G. Perkin ¹⁰ has prepared are also to be included in this group:

Dye.	HCl	HBr	HI	H ₂ SO ₄
Myricetine C ₁₅ H ₁₀ O ₈	+	+	+	+
Quercetine C ₁₅ H ₁₀ O ₇	+	+	+	+
Rhamnetine $C_{16}H_{12}O_7$				+
Rhamnazine $C_{17}H_{14}O_7$			2-1	+
Morine $C_{15}H_{10}O_7$	+	+	+	+
Luteoline $C_{15}H_{10}O_6$	$+ H_2O$	$+ H_2O$	+	+
Luteoline $C_{15}H_{10}O_6$ Fisetine $C_{15}H_{10}O_6$	+	+	+	+

The oxonium salts formed by the addition of orthophosphoric acid and arsenic acid to ketones are very interesting; examples of these are:

$$\begin{bmatrix} C_{6}H_{2}(CH_{3})_{3} \\ | \\ COCH_{3} \end{bmatrix} H_{3}PO_{4} \quad and \quad [H_{4}C_{6}(COCH_{3})_{2}](H_{3}PO_{4})_{2}^{-1}$$

¹ Klages and Allendorf, Ber., 31, 1298 (1898); 32, 1569 (1899).

The same may be said of the salts of phosphine 11 and aminoxyde. 12

¹ Dumas and Péligot, Bull. Soc. Chim., 24, 160, 241 (1875).

² Kékulé and Fleischer, Ber., 6, 936 (1873).

³ Fischer, Annalen, 183, 68 (1876).

⁴ Baeyer, *ibid.*, p. 27. ⁵ Dale and Schorlemmer, *ibid.*, 196, 84 (1879).

⁶ Claisen and Ponder, ibid., 223, 142 (1884).

⁷ Wallach, ibid., 246, 281 (1888).

⁸ Collie and Tickle, Trans., 75, 710 (1899). 9 Ber., 34, 2979 (1901).

¹⁰ Trans., 72, 1439 (1896). 11 Pickard and Kenyon, Trans., 89, 262 (1906).

¹² Willstätter, Ber., 33, 1636 (1900).

(b) The Ammonium Salts.

Since it has been shown already that ammonia and amines link themselves, by means of one of the auxiliary valencies on the nitrogen atom, to the central atom of oxides, halides, salts, etc., of the most diverse elements, then it is to be expected that they will combine in like manner with the hydrogen atoms of certain hydrogen compounds. It is hardly necessary to say that this anticipation has been fulfilled, for these addition-compounds are well known. The only point under discussion is the question as to whether these new ideas will not provide a more satisfactory constitutional formula for the ammonium salts than the old ones were able to do.

The supporters of the theory of constant valency considered the ammonium salts purely as molecular compounds, i.e. compounds in which the molecular components retained their integrity, and were not combined together by atomic valencies. This conception can be formulated by the symbol

$$[(\mathbf{H}_3\mathbf{N})\ (\mathbf{HCl})]$$

Nowadays the formation of ammonium salts, e.g. ammonium chloride, is explained quite often by supposing that the principal valencies of nitrogen undergo an increase; in other words, it is supposed that the trivalent nitrogen of ammonia becomes pentavalent and links to itself both components of hydrochloric acid by means of these additional valencies. This idea finds expression in the equation:

$$\mathbf{H}_{\mathbf{H}} = \mathbf{H}_{\mathbf{H}} =$$

But the ideas which have been developed in the foregoing pages lead to the following explanation. The nitrogen of ammonia still contains an unsaturated auxiliary valency, which can be saturated by an auxiliary valency of the hydrogen atom in hydrochloric acid. The formation of ammonium chloride is therefore illustrated by the equation:

$$H \rightarrow N + HCl = H \rightarrow N \dots HCl$$

Since, according to this formula, four hydrogen atoms are bound to nitrogen, it is hardly to be supposed that one hydrogen atom is linked up by a greater amount of affinity than any of the remaining three; it is far more probable that a state of equilibrium is reached in which all the hydrogen atoms are linked by the same amount of affinity. Ammonium is therefore a complex radicle, NH₄, in which the central nitrogen atom links the four hydrogen atoms to itself by the same amount of affinity in each case. On each hydrogen atom of the complex NH₄ there is still a certain amount of unsaturated affinity, which the radicle is able to utilize external to itself and becomes in this way monovalent. Ammonium salts have therefore the following structural formula:

$$\begin{bmatrix} \mathbf{H} : \mathbf{N} : \mathbf{H} \end{bmatrix} \mathbf{X}$$

The different formulæ which have been proposed for ammonium chloride consequently are as follows:

$$(\mathbf{H}_3\mathbf{N})(\mathbf{HCl}), \qquad \mathbf{H}_3\overset{\mathbf{V}}{\mathbf{N}} < \overset{\mathbf{H}}{\mathbf{Cl}}, \qquad \begin{bmatrix} \mathbf{H} : \mathbf{N} : \overset{\mathbf{H}}{\mathbf{H}} \end{bmatrix} \mathbf{Cl}.$$

Molecular formula Valency formula Auxiliary valency formula

It is well known that the controversy as to whether the ammonium salts were to be classed as molecular or valency compounds was of long duration, but finally concluded in favour of the valency formula. But the very fact that it was a long controversy shows that the question is by no means a simple one. However, with the object of offering a final solution to this problem, which appears once more under quite a new guise, all the physical-chemical and chemical behaviour of the ammonium salts must be passed under review.

The properties of the organic ammonium salts and of the quaternary bases are so contrary to what would be expected were ammonium salts molecular complexes of indefinite constitution that the first formula is quite untenable. Consequently, only the valency and auxiliary valency formulæ remain to be discussed.

It may be noted that the chief argument used for the valency formula, viz. the direct attachment to the nitrogen of all the alkyl residues in the tetraalkyl ammonium salts, can, with equal advantage, be used to support the auxiliary valency formula.

Against the ammonium theory as accepted at present, and for the auxiliary valency theory, the following arguments may be brought

forward. Firstly, the so-called fifth valency of nitrogen, the properties of which are supposed to be like those of the alkali valencies, can offer no explanation for such behaviour, for the supposition that the fifth valency has such properties is only a periphrasis of the fact. Further, when it is remembered that in order to be consistent this behaviour must be looked for in all those compounds which display abnormal valencies, i.e. phosphonium, oxonium, thionium, and iodonium salts, etc., and in the supplementary valencies of phosphorus, oxygen, sulphur, and iodine, then it is difficult not to feel that the assumption is very improbable. An ammonium theory having such an assumption for its foundation could have been retained only until a better explanation for the phenomena was offered.

The inadequacy of the ammonium theory which requires nitrogen to be pentavalent is clearly seen in the hesitating way in which use is made of these latter consequences, and in many cases they are not used to explain those chemical reactions which certainly are analogous to the formation of ammonium salts. This is particularly noticeable in the formulæ which are used to explain the formation of double salts (double halides). Thus when antimony trichloride takes up one molecule of potassium chloride the reaction is certainly analogous to the formation of ammonium chloride, and consequently should be formulated in a similar way:

$$\frac{N}{R_3} + IR = \frac{I \cdot N \cdot R}{R_3}$$
, $\frac{Sb}{Cl_3} + ClK = \frac{Cl \cdot Sb \cdot K}{Cl_3}$

But when this practice is consistently and logically carried out, the valency of the central atom sometimes attains a surprisingly high value, as in the compounds ferro- and ferricyanide of potassium:

Should consistency in this way be obtained, it would be of little value, for these formulæ are unable to explain the remarkable agreement in the composition of the maximum types of complex salts belonging to the most diverse elements. Moreover, in common with all other formulæ of compounds containing components

which dissociate electrolytically, their structure cannot be proved directly, because nothing certain can be said of the position in the molecule to which dissociating radicles are joined. It must, therefore, be quite clearly understood that those methods which are in use at present, give just as little idea of the position in the molecule occupied by the potassium atoms as they do of the position occupied by the acid residue in ammonium salts. When it is desired to determine the constitution of such compounds, derivatives must be prepared which are electrically undissociated. As a matter of fact, such derivatives of potassium ferrocyanide do exist, i.e. the esters of ferrocyanic acid, and their chemical behaviour shows that the organic residue is not linked to the iron but rather to the cyanide group. This is true, both of the ethyl ester prepared by Freund, and also of the phenyl ester which Bamberger 2 prepared.

In the very few cases in which it is possible to carry out an experimental verification of such constitutional formulæ, the results are contrary to the ammonium theory.

A further disadvantage of the ammonium theory is seen in the fact that it does not allow the formation of ammonium salts and of the simple metallic ammino-complexes to be analogously formulated. Similarly, although the addition of ammonia to an acid and to a metallic chloride,

 $ClH + NH_3 = ClH \cdot NH_3$ $Cl_2Pt + 2NH_3 = Cl_2Pt \cdot (NH_3)_2$

are completely analogous reactions. In this way is lost a relationship which is of importance, for it renders possible a method for the consistent formulation of the most diverse ammonium salts.

Again, the customary ammonium formula can give only a forced explanation of the process of electrolytic dissociation. Nowadays it is almost universally accepted that the electrical charge on a monovalent, polyatomic ion is localized on a definite atom, for only in this way is it possible to reconcile this idea with the modern atomistic conception of unit charges. Then, when providing the ammonium salts with pentavalent nitrogen, it must be assumed that their electrical charge is transferred during formation from the hydrogen to the nitrogen; in other words, against all

¹ Ber., 21, 935 (1888).

² Ibid., 26, 480 (1893).

³ In this compound both chlorine atoms are non-ionogene, and consequently must be in direct attachment with the platinum atom.

previous observations it is implied that negative nitrogen has a greater tendency to assume a positive character than positive hydrogen. It is hardly necessary to say that this is highly improbable.

All these difficulties make it clear that the present ammonium theory is unsatisfactory. In what follows it will be shown that these and other difficulties resulting from the theory of pentavalent nitrogen give way before the new ammonium theory.

The auxiliary valency formula presupposes that all four hydrogen atoms are linked directly to nitrogen—a supposition which the constitution of the tetraalkyl ammonium compounds confirms. This theory corresponds to the experimental results at least as well as the older formula. But the present theory is better than the older one, because it clears up the difficulty, without introducing any new hypothesis, which arises from the behaviour of the acid residue in the ammonium salts. For on considering the following formula for ammonium chloride

$$\begin{bmatrix} \mathbf{H} & \mathbf{N} & \mathbf{H} \\ \mathbf{H} & \mathbf{N} \end{bmatrix}$$
Cl

it is evident that the chlorine of the hydrochloric acid undergoes no change in its linking when it becomes attached to the nitrogen atom. Consequently the functions of the chlorine in ammonium chloride and also in hydrochloric acid are quite comparable to the behaviour of the chlorine in platosammine chloride,

and plato chloride, PtCl₂, for in the latter case the entrance of ammonia into the molecule does not affect the dissociation-constant of plato chloride, and therefore it is only reasonable to expect this to be true of the combination of ammonia with hydrochloric acid—a fact, as is well known, which experiment confirms. And since the hydrogen can no longer appear as hydrion it confers its character upon the ammonium radicle as a whole. Consequently, the auxiliary valency formula offers, without making any additional suppositions, an explanation for the new properties of the molecular components of the ammonium salts.

If the formation in solution of ammonium chloride from ammonia and hydrochloric acid is represented by the equation,

$$H_3N + \dot{H} + \dot{Cl} = (NH_4)^+ + \dot{Cl},$$

then the corresponding formation of ammonium hydroxide from ammonia and water will be represented by

$$H_3N + \dot{H} + O\dot{H} = (NH_4)^+ + O\dot{H},$$

or in other words, ammonium hydroxide is to be considered as the addition-product of ammonia and hydrion of water.

This idea explains the enormous increase in electrical conductivity which water undergoes on the solution of ammonia. An aqueous solution of ammonia bears to a solution of ammonium salts the same relationship that water bears to a solution of hydrochloric acid. Aqueous ammonia and water are bad conductors, and solutions of ammonium chloride and hydrochloric acid are good conductors.

Again, this ammonium theory does not require it to be supposed that the positive electric charge on the hydrogen atom is transferred to the negative nitrogen atom.

From what has already been said, it will be obvious that the auxiliary valency theory is better able to explain the facts of the chemistry of ammonium compounds than that which makes nitrogen pentavalent. Its superiority is even more evident in the manner in which it brings out the relationship between the ammonium salts and the metallic ammino-complexes—a relationship which the older theory is quite unsuited for giving expression to. But beyond this, the auxiliary valency formula is the only one which can provide a simple explanation for the so-called "anomalous" ammonium salts. These compounds result when the hydrogen of the acid takes up not only one but two molecules of ammonia. The following equation makes clear the reaction by which "anomalous" ammonium salts are formed,

$$XH + 2NR_3 = X \cdot H \begin{cases} NR_3 \\ NR_3 \end{cases}$$

This equation is quite as characteristic for certain classes of derivatives of ammonia as that describing the formation of simple ammonium salts:

$$XH + NR_3 = \left[N_H^{R_3}\right]X$$

from ammonia and simple amines.

We have to thank Wheeler and his pupils for our knowledge of a great many of such anomalous ammonium salts; the author 1 has collected the references and recently published an entire list of them. Thus the following anomalous ammonium salts of simple amines are known:

$$\begin{split} 2NH_3 \,.\, HBr,^1 \quad & Py_2 \,.\, HBr_5, \quad (NH_2OH)_2 \,.\, HCl,^2 \quad (sec. \ C_4H_9NH_2)_2HI,^3 \\ (tert. \ C_4H_9NH_2)_2HI,^3 \quad & \left(C_5H_{11}NH_2\right)_2HI,^3 \quad \left[\begin{matrix} CH \\ C_{10}H_6 \\ NH \end{matrix}\right] CH \\ & \left[\begin{matrix} CH \\ CH \end{matrix}\right]_2HCl,^4 \\ & \left[\begin{matrix} C_7H_9N \end{matrix}\right]_2HCl,^5 \quad (NH_2OH)_2HI,^6 \quad (NH_2OH)_3HI,^6 \\ & \left(C_4H_8ON)_2HCl, \quad (C_4H_8ON)_2HBr.^7 \end{matrix} \end{split}$$

¹ Rec. d. trav. chim. d. Pass-Bas., 4, 361 (1885).

² Annalen, 84, 242 (1852).

³ Rudnew, J. pr. Chem., 46, 305 (1849).

4 Annalen, 247, 305 (1888).

5 Ibid., 239, 240 (1887).

⁶ Dunstan and Goulding, Trans., 69, 839 (1896).

" Pyrolidon salts," Tafel and Wasmuth, Ber., 40, 2834 (1907).

It is distinctly worthy of note that compounds are known in which more than two molecules of ammonia are linked to acid hydrogen; the following have been definitely characterized:

$$(H_3N)_4$$
. HCl_1^1 $(H_3N)_4HBr_2$ and $(H_3N)_3$. HNO_3^2

Joannis, Compt. rend., 135, 1106 (1902).
 Zeitsch. physikal. Chem., 25, 108 (1898).

The existence of anomalous ammonium salts shows that one of the hydrogen atoms in such salts, as a result of its unsaturated character, can play the same part as the metallic atoms in the metallic ammino-compounds, and is consequently functionally different from the remaining hydrogen atoms.

The following conclusion may be drawn from the foregoing discussion: All the properties of the ammonium salts are consistently explained by the auxiliary valency formula, and that in all those cases in which the pentavalent theory of nitrogen leads to untenable results or requires the aid of improbable hypotheses, the auxiliary valency formula simply and clearly explains the experimental facts. Hence we conclude that the ammonium compounds

are not derived from pentavalent nitrogen, but correspond rather to the following formula:

$$\begin{bmatrix} \mathbf{H} & \mathbf{H} \\ \mathbf{H} & \mathbf{H} \end{bmatrix} \mathbf{X}$$

In his chapter on ammonium in Abegg's Handbuch der Anorganischen Chemie (vol. iii.), v. Braun has shown in a masterly way how simply and consistently all the facts of ammonium chemistry may be explained when using this formula.

9. Theory of Bases and Acids. (a) Theory of Bases.

1. The Hydroxometallic Ammino Salts.

(a) Introduction.

The hydroxometallic ammino salts are a group of salts which are of considerable theoretical importance, and one which during the last few years has been thoroughly examined. The members of this group contain in the complex hydroxyl linked directly to the central atom, as, for example, the hydroxopentammine cobalti salts:

$$\begin{bmatrix} OH \\ Co \\ (NH_3)_5 \end{bmatrix} X_2$$

Pfeiffer, while working on chromium compounds, was the first to recognize the existence of this class of compound. He showed that they formed salts by the addition of acids, and were regenerated by splitting off the acids, thus:

I was then able to show that such hydroxo salts were formed by the ammino salts of cobalt, ruthenium, and platinum. A comparative examination of these compounds caused me to extend considerably the theory of bases. These changes are set forth in the following sections.

¹ Pfeiffer, "Über eine neue Klasse salzbildender Metallhydroxyde," Ber., 31,1864 (1906).

(b) Properties of the Hydroxometallic Ammoniates.

The examination of the following hydroxo series:

$$\begin{bmatrix} HO \\ O_2N Co(NH_3)_4 \end{bmatrix} X,^1 \quad \begin{bmatrix} Co_{(NH_3)_5}^{OH} \end{bmatrix} X_{2^3}^2 \quad \begin{bmatrix} HO \\ H_2O Co(NH_3)_4 \end{bmatrix} X_{2^3}^3$$

$$\begin{bmatrix} (1)HO \\ (2)H_2O Co en_2 \end{bmatrix} X_{2^4}^4 \quad \begin{bmatrix} (1)HO \\ (6)H_2O Co en_2 \end{bmatrix} X_{2^5}^5 \quad \begin{bmatrix} HO \\ H_2O Cr_{(NH_3)_2}^{(OH_2)_2} \end{bmatrix} X_{2^5}^6$$

$$\begin{bmatrix} HO \\ HO Cr_{(NH_3)_2}^{(OH_2)_2} \end{bmatrix} X,^7 \quad \begin{bmatrix} HO \\ H_2O Co_{(NH_3)_2}^{Py_2} \end{bmatrix} X_{2^8}^8 \quad \begin{bmatrix} HO \\ HO Ru(NH_3)_4 \end{bmatrix} X_{2^9}^9$$

$$\begin{bmatrix} HO \\ HO Cr_{(NH_3)_4}^{OH_3} \end{bmatrix} X,^7 \quad \begin{bmatrix} HO \\ H_2O Co_{(NH_3)_4}^{Py_2} \end{bmatrix} X_{2^8}^8 \quad \begin{bmatrix} HO \\ HO Ru(NH_3)_4 \end{bmatrix} X_{2^9}^9$$

- ¹ Werner, Ber., 40, 4117 (1907).
- ² Ibid., 4098 (1907).
- 3 Ibid., 4113 (1907).
- 4 Ibid., 272 (1907).
- ⁵ Ibid., 272 (1907).
- 6 Werner and Dabsky, ibid., 4092 (1907).
- 7 Ibid., 4085 (1907).
- ⁸ Werner, ibid., 468 (1907).
- 9 Ibid., 2614 (1907).
- 10 Ibid., 2614 (1907).

has yielded the results given below:-

1. Behaviour towards Silver Nitrate.

Only the salts in the first series are able to precipitate silver oxide from a solution of silver nitrate.

2. Behaviour towards Litmus.

The salts belonging to the first eight series of compounds react alkaline; those of the first series are strongly alkaline, the remaining are only weakly alkaline. The members of the ninth and tenth series are neutral.

3. Behaviour towards Ammonium Salts.

Those salts which belong to the first three series liberate ammonia, in the cold, from ammonium salts, thereby passing into aquo salts. The members of the remaining series have not got this property.

4. Behaviour towards Carbon Dioxide.

The salts of the first five series absorb carbon dioxide, thus becoming carbonato-salts; the members of the first series exhibit this property most strongly. The salts of the last five series do not absorb carbon dioxide.

5. Behaviour towards Acetic Acid.

The salts of the first eight series are more soluble in acetic acid than in water. On solution they are transformed into aquo salts. From solutions of 1, 2, and 3 metallic salts precipitate aquo salts, but from 4, 5, 6, 7, and 8, hyroxo salts are again precipitated. The salts of 9 and 10 do not form aquo salts with acetic acid, and they are therefore no more soluble in acetic acid than in water.

6. Behaviour towards Mineral Acids.

All the series form aquo salts with mineral acids. This tendency is weakest in the last series, which, although two hydroxyl groups are in the molecule, only take up one molecule of hydrochloric acid. From the hydrochloric acid solutions of series 1 to 8 aquo salts are usually precipitated by metallic salts; but certain reagents will precipitate hydroxo salts in series 4 to 8. The salts of series 9 and 10 are always precipitated from acid solution as hydroxo salts.

From these considerations it is evident that the hydroxo salts exhibit great differences amongst themselves in aqueous solution, and display all possible stages between the strongly basic hydroxonitrotetramminecobalti salts up to the completely neutral dihydroxotetrammineplatinum salts.

(c) On the Condition of the Hydroxometallic Ammoniates in Aqueous Solution.

The examination of the metallic ammino-complexes has shown that in the anhydrous forms the acid residue is directly linked to the central atom, but in the hydrated forms it is ionized. The formation of hydrates is consequently the first action that takes place on the electrolytic dissociation of a salt in aqueous solution:

$$\left[Co_{(\mathbf{NH}_3)_5}^{\mathbf{Cl}}\right]Cl_2 + H_2O \rightarrow \left[Co_{(\mathbf{NH}_3)_5}^{\mathbf{OH}_2}\right]Cl_3$$

Chloro salt
(One chlorine atom undissociated) (All chlorine atoms dissociated)

These hydroxo-compounds behave just like the other metallic ammino-complexes, i.e. the hydroxyl directly attached to the metallic atom remains undissociated, and the electrolytically dissociated portion of the hydroxo-compound is present in aqueous solution as the hydroxide of an aquo-compound:

$$\begin{bmatrix} \text{Co}_{(\text{NH}_3)_5}^{\text{OH}} \end{bmatrix} \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \begin{bmatrix} \text{Co}_{(\text{NH}_3)_5}^{\text{OH}_2} \end{bmatrix} \text{OH} \\ \text{Hydroxo-compound} \\ \text{(Hydroxyl undissociated)} \qquad \qquad \begin{matrix} \text{Aquo-compound} \\ \text{(Hydroxyl dissociated)} \end{matrix}$$

This conception is founded on the following observations:—

That the hydroxyl-compound as such is present in solution is evident from the fact that it is possible to salt it out by the addition of metallic salts.

The absorption of carbon dioxide is a further argument for the existence in solution of unchanged hydroxo-compound; for the carbonato-salts which result from this absorption are to be considered as being produced by direct addition of carbon dioxide to the hydroxyl group in the hydroxo-complex:

$$\left[Co_{(\mathbf{NH}_{3})_{5}}^{\mathbf{OH}}\right]X_{2} + CO_{2} = \left[Co_{(\mathbf{NH}_{3})_{5}}^{\mathbf{O} \cdot \mathbf{CO}_{2}\mathbf{H}}\right]X_{2}$$

Hence it follows that in solutions of all hydroxo salts, including those which are most strongly basic, unchanged hydroxo-compounds must be present.

On the other hand, the simultaneous presence of aquo-compounds is argued from the following facts:—

All the hydroxo-compounds are transformed into aquo-compounds by the addition of acids to their solutions, thus:

$$\left[Co_{(NH_3)_5}^{OH}\right]^{++} + \overline{X}_2 + (H + \overline{X}) = \left[Co_{(NH_3)_5}^{OH_2}\right]^{+++} + 3\overline{X}$$

and the quantity of aquo salts, which is formed depends upon the strength of the acids and the concentration of hydrion. Further, since water itself is partly ionized it follows that the formation of aquo-bases must also take place in aqueous solution:

$$\left[Co_{(NH_3)_5}^{OH}\right]^{++} + \overline{X}_2 + (H + OH) = \left[Co_{(NH_3)_5}^{OH}\right]^{+++} + 2\overline{X} + OH$$

It may be asked, is it not possible that a certain amount of the hydroxo-compound exists in solution in a dissociated but not hydrated condition? The answer to the question is, that nothing supports such a supposition. Against the idea, however, it may be urged, that the action of acids on dissolved hydroxo-compounds never yields those anhydrous compounds which would be given were such salts present, but always aquo-salts.

Consequently it is to be concluded that only two types of compounds are present, namely, the hydroxo-compounds as such, and their hydration products, the aquo-bases, and further, that of these two types of compounds only the aquo-salts behave as true bases, i.e. they dissociate in solution yielding hydroxyl ions. The hydroxo-compounds are related to the aquo-compounds in the same way that ammonia is related to ammonium hydroxide. They are therefore basic anhydrides, and, in order to avoid confusion, they will be termed Anhydrobases, and the products of their hydration Aquobases.

2. Generalization of the Results.

(a) Application to Metallic Hydroxides.

The hydroxometallic ammino-complexes are members of the great group of metallic hydroxides. They differ from most of the other metallic hydroxides only in the fact that, on account of their peculiar constitution (the occupation of most of the co-ordination positions of the metallic atoms by ammonia or amines, which, however, do not take part in the chemical changes), they are most suited for experimental examination. A difference in principle in the behaviour of those metallic hydroxides which contain ammonia and those which are ammonia-free appears very improbable. Consequently it must be possible, from the results obtained from the study of the metallic hydroxides which contain ammonia, to formulate a general theory for the behaviour of metallic hydroxides in general.

Metallic hydroxides are usually defined as bases, and by the term "base" is understood hydroxyl-compounds, which in aqueous solution dissociate into a positive ion and a hydroxyl ion.

In this definition it is assumed that the hydroxyl ions in solution are produced by the detachment of the hydroxyl groups linked to the metallic atoms. This conception, according to which the metal and hydroxyl separate, is not in keeping with the observations made on hydroxo-metallic ammino-complexes. The metallic hydroxide as such, e.g. ferric hydroxide, magnesium hydroxide, calcium hydroxide, potassium hydroxide, etc., are not compounds which dissociate directly, but rather are anhydro-bases, from which, by the addition of water, the true base (aquo-base) is produced. Consequently we must differentiate between two types of compounds not only in the

hydroxometallic ammino-complexes, but in general: (a) metallic hydroxides as such, which are the anhydro-bases; and (b) aquometallic hydroxides, which are dissociated electrically and are the true bases.

(b) General Definition of a Base.

According to what has been said, then, the metallic hydroxides are related to the true base in the same way that ammonia is to ammonium hydroxide, or phosphoretted hydrogen to phosphonium hydroxide, etc. Metallic hydroxides, ammonia, and phosphine are anhydro-bases; but, on the other hand, aquometallic hydroxides, ammonium hydroxide, and phosphonium hydroxide, etc., are the aquo- or true bases. From these considerations the following definitions are obtained. 1. A difference must be made between Anhydro-bases and Aquo-bases. 2. Every compound which combines with water to form a hydrate, which, in its turn, dissociates in aqueous solution into a complex positive ion and hydroxyl ions, is an anhydro-base. 3. Aquo-bases, or shortly bases, are all addition-compounds with water which form hydroxyl ions in aqueous solutions.

(c) Subdivisions of Anhydro-bases.

According to the element to which the water atom attaches itself will it be possible to form sub-groups of the anhydro-bases. Such would be nitrogen, oxygen, phosphorus anhydro-bases, etc. To the oxygen anhydro-bases belong all those oxygen compounds of the metals and all the organic oxygen compounds which form oxonium salts. In this class must be included also all the quaternary ammonium, phosphonium, and arsonium bases, and further the sulphonium, iodonium, and tertiary oxonium bases, all of which are comparable to the metallic hydroxides:

R₄N.OH, R₄P.OH, R₃S.OH, R₂I.OH, R₃O.OH

To the nitrogen anhydro-bases belong ammonia, amines, and certain metallic amides, etc.; to the phosphorus anhydro-bases phosphoretted hydrogen, the phosphines, etc. Finally, it must not be forgotten that the most varied elements can appear in their compound as anhydro-bases.

- 3. On the Behaviour of Aquometallic Hydroxides on Salt Formation.
 - (a) On the formation of Anhydro-salts from Aquo-bases.

According to the new theory of bases, it is to be expected that basic metallic hydroxides and analogous compounds would always form aquo-salts when neutralized with acids:

$$\begin{bmatrix} \mathbf{K} \\ \mathbf{H} \\ \vdots \\ \mathbf{O} \\ \cdot \mathbf{H} \end{bmatrix} \mathbf{O} \mathbf{H} + \mathbf{H} \mathbf{X} = \begin{bmatrix} \mathbf{K} \\ \mathbf{H} \\ \vdots \\ \mathbf{O} \\ \cdot \mathbf{H} \end{bmatrix} \mathbf{X} + \mathbf{H}_{2} \mathbf{O}$$
$$\begin{bmatrix} \mathbf{R}_{4} \mathbf{N} \\ \mathbf{H} \\ \vdots \\ \mathbf{O} \\ \cdot \mathbf{H} \end{bmatrix} \mathbf{O} \mathbf{H} + \mathbf{H} \mathbf{X} = \begin{bmatrix} \mathbf{R}_{4} \mathbf{N} \\ \mathbf{H} \\ \vdots \\ \mathbf{O} \\ \cdot \mathbf{H} \end{bmatrix} \mathbf{X} + \mathbf{H}_{2} \mathbf{O}$$

Although, as a matter of fact, most hydroxo-metallic amino-complexes form aquo-salts and a similar behaviour can be proved in the case of certain ammonia-free hydroxo-compounds, e.g.

$$\frac{\mathrm{HO}}{\mathrm{HO}} \left[\frac{\mathrm{H_2O}}{\mathrm{H_2O}} \mathrm{Cr}(\mathrm{OH_2})_4 \right] \mathrm{X} + 2\mathrm{XH} = \left[\frac{\mathrm{H_2O}}{\mathrm{H_2O}} \mathrm{Cr}(\mathrm{OH_2})_4 \right] \mathrm{X}_3 + 2\mathrm{H_2O}$$

yet it should be noted that anhydrous salts are often obtained on neutralizing metallic hydroxides with acids. A disagreement consequently exists between the behaviour to be expected according to theory and that which experiment reveals. This disagreement, however, is only apparent, as can easily be proved from certain observations made on some metallic ammino-complexes.

With reference to the stability and existence of aquo-salts, the following has been proved. All the hydroxo-salts in the series already given (p. 201), as far as they possess the property of forming aquo-bases, yield aquo-salts which have been obtained in the solid state. But it also has been shown that there is a regular gradation in the stability manifested by these aquo-salts. This will be discussed under the aquo-chlorides.

The most stable chloride in this series is aquonitrosotetramminruthenium chloride, for it is only transformed into the anhydro-salt
on long heating with hydrochloric acid. Diaquodipyridinediammir
cobalt chloride is almost as stable. On the other hand, the aquochlorides in series 4 to 7 pass into chloro-compounds on standing
for a long time in cold hydrochloric acid, while aquopentammine
cobalt chloride and diaquotetrammine cobalt chloride are transformed
by simply leaving a concentrated solution of these salts to stand.
Nevertheless all these aquo-chlorides are sufficiently stable to be
precipitated unchanged on the addition of hydrochloric acid to their
aqueous solutions.

Very different behaviour is exhibited by the aquo-series of the strong bases, derived from the hydroxonitrotetrammine salts. For anhydro-salts are precipitated from aqueous solutions on the addition of hydrochloric acid, and even by potassium chloride, so that the aquo-chloride

$$\begin{bmatrix} O_2 \mathbf{N} \\ \mathbf{H}_2 \mathbf{O} \mathbf{Co} (\mathbf{N} \mathbf{H}_3)_4 \end{bmatrix} \mathbf{Cl}_2$$

cannot be prepared by this method. It may, however, be prepared by another method, but the salt is so unstable that, on keeping for a short time, it passes into the anhydro-salt. The water in the nitroaquotetrammine cobalti radicle,

$$\begin{bmatrix} O_2 \mathbf{N} \\ \mathbf{H}_2 \mathbf{O} \mathbf{Co} (\mathbf{N} \mathbf{H}_3)_4 \end{bmatrix}$$

is consequently so labile, that the existence of the aquochloride can only be shown under special conditions, and in the following case it is quite impossible to obtain the aquochloride. Chlorodinitrotriammine-cobalt,

$$\begin{bmatrix} \operatorname{Cl}_{(\mathrm{O_2N})_2} \operatorname{Co}(\mathrm{NH_3})_3 \end{bmatrix}$$

is an intensely red compound, which slowly, but in great quantities, dissolves in water, giving a yellow solution and forming the aquocompound. From this solution the addition of potassium chloride always precipitates the anhydrous compound. On treating the chloride with silver oxide, a solution of the base is obtained, which is so strongly alkaline that it immediately precipitates silver oxide from a solution of silver nitrate.

These facts prove that the instability of the free aquo-salts in no way contradicts the assumption of the existence of aquo-bases and aquo-salts in solution, but shows rather that a relationship exists between the strength of the base and the stability of the aquo-salts; for the stability decreases as the strength of the base increases. Consequently the phenomenon that the strongest metallic hydroxide bases, e.g. those of the alkali metals, preferably yield anhydrous salts, is to be explained by the assumption that the aquo-salts, which are primarily formed, are too unstable to exist.

(b) On the Influence of the Nature of Acids and Bases on the Stability and Existence of Aquo-salts.

The greater or less stability of the aquo-salts will depend, on the one hand, upon the strength with which the water is bound in the

molecule, and, on the other hand, on the tendency of the acid residue to form the anhydrous salt. Since this tendency is dependent upon the nature of the basic and acid radicle, it follows that the stability of the aquo-salt varies with the nature of the acids and bases of which it is composed. Experiment confirms this prediction, but the results cannot be discussed here, since it would take up too much space.¹

4. On the Genetical Relations between Anhydro-bases and Aquo-bases.

In solutions of metallic hydroxides are to be found simultaneously the non-dissociated anhydro-base and the dissociated hydrated base; it is therefore of interest to know what are the genetic relations of these two compounds. This is obtained from the following considerations. The aquo-salts yield, as has been experimentally shown, two types of compound, namely, the anhydroform, produced by the substitution of water in the molecule, thus:

$$\left[\mathrm{Co_{(NH_3)_5}^{Cl}}\right]\!\mathrm{Cl_2} + \mathrm{H_2O} = \left[\mathrm{Co_{(NH_3)_5}^{OH_2}}\right]\!\mathrm{Cl_3}$$

and the form produced by the addition of acids to the anhydro-base, thus:

$$\left[\mathrm{Co_{(NH_3)_5}^{OH}}\right]\!\mathrm{Cl_2} + \mathrm{HCl} = \left[\mathrm{Co_{(NH_3)_5}^{OH_2}}\right]\!\mathrm{Cl_3}$$

Corresponding to these equations, aquobases may be formed theoretically in two different ways; they may be produced either by the substitution or by the addition of water, thus:

$$\begin{bmatrix} \text{Co}_{(\text{NH}_3)_5}^{\checkmark} \end{bmatrix} \text{Cl}_2 + \text{OH}_2 = \begin{bmatrix} \text{Co}_{(\text{NH}_3)_5}^{\text{OH}_2} \end{bmatrix} \text{OH}_2 \\ \begin{bmatrix} \text{Co}_{(\text{NH}_3)_5}^{\text{OH}_2} \end{bmatrix} \text{Cl}_2 + \text{H} \cdot \text{OH} = \begin{bmatrix} \text{Co}_{(\text{NH}_3)_5}^{\text{OH}_2} \end{bmatrix} \text{OH}_2 \\ \begin{bmatrix} \text{Co}_{(\text{NH}_3)_5}^{\text{OH}_2} \end{bmatrix} \text{Cl}_2 + \text{H} \cdot \text{OH} = \begin{bmatrix} \text{Co}_{(\text{NH}_3)_5}^{\text{OH}_2} \end{bmatrix} \text{OH}_2 \\ \end{bmatrix}$$

The first equation supposes that the reaction takes place, through the loosening of an oxygen-metallic linking in order that a similar linking may again be formed. Such an assumption is very improbable, and all the more so since the same result, *i.e.* the formation of the aquobase, can be brought about much more simply by the addition of water to the hydroxyl group. A further argument

¹ Cf. Werner, Ber., 40, 4140 (1907).

for the second equation is that it is the more probable from the electric standpoint, thus:

$$\left[Co_{(NH_3)_5}^{OH}\right]^{++} + 2\bar{C}l + \left(\dot{H} + \bar{OH}\right) = \left[Co_{(NH_3)_5}^{OH_2}\right]^{+++} + 2\bar{C}l + \bar{OH}$$

For it is difficult to understand why the active hydrogen ions should take no part in the reaction, while the inactive, undissociated water molecules played the chief $r\hat{o}le$. The formation of aquobases, then, takes place according to this last equation, and anhydrobases consequently can be defined in the following words: Anhydrobases are compounds which, in aqueous solution, combine with the hydrion of water, and in this way disturb the dissociation equilibrium of water until the concentration of the hydroxylions reach that value which is characteristic for the compound.

5. On the Strength of Bases.

The process by which aquo-salts are formed from hydro-compounds and acids is a reversible one, and may be formulated thus:

$$\left[Co_{(\mathbf{NH}_3)_5}^{\mathbf{OH}_2}\right]Cl_3 \iff \left[Co_{(\mathbf{NH}_3)_5}^{\mathbf{OH}}\right]Cl_2 + HCl$$

The equation towards the right gives expression to the phe nomena of hydrolysis, and receives attention in a later paragraph. The formation of aquo-bases is also reversible:

$$\left[Co_{(\mathrm{NH_3})_5}^{\mathrm{OH_2}}\right]_{\mathrm{Cl_2}}^{\mathrm{OH}} \leftrightarrows \left[Co_{(\mathrm{NH_3})_5}^{\mathrm{OH}}\right]_{\mathrm{Cl_2}} + \mathrm{H_2O}$$

From this it follows that the production of anhydro-bases from aquo-bases is a hydrolytic reaction, the value of which depends upon the strength of the base; for the more trifling the hydrolysis, the stronger will be the base. Consequently the quantity of aquo-base formed chiefly depends upon the concentration of hydrion and the affinity of the base-forming element for hydrion. Since the electrolytic dissociation of water is small it would only be possible for large quantities of the dissociated base to be formed, when the base-forming element displays great affinity for hydrion. That this property is of great importance to the strength of the base, can be convincingly demonstrated by examples of the following description.

E. 1361

The series of compounds corresponding to the formulæ,

$$X_2[(H_3N)_4Co_{NH_3}^{OH}]$$
 X

Hydroxopentammine salts Hydroxopentament

$$X[(H_3N)_4Co_{NO_3}^{OH}]$$

Hydroxonitrotetrammine salts

$$X_2 \left[(H_3N)_4 Co_{OH_2}^{OH} \right]$$

Hydroxoaquotetrammine salts

$$\begin{bmatrix} (\mathbf{H_3N})_3 \mathbf{Co_{NO_2}^{OH}} \end{bmatrix}$$

Hydroxodinitrotetrammine salts

have been examined to test their basic character.

The presence of the strongly negative nitro-residues in the complex radicles of the two latter salts would lead one to expect that the basic character of their hydroxyl groups would be weaker than those in the two former salts. In reality, however, the two latter salts are much stronger bases than the former pair, for the complexes containing the nitro-groups precipitate silver as oxide from silver nitrate solutions, while the complexes in which the nitro-group is absent are unable to do so.

From these facts it is evident that the basic character of these compounds depends to a great extent upon the affinity of the complex for hydrion. The same is true of the complex organic bases, as the quaternary ammonium, phosphonium, sulphonium, and iodonium bases, in which the positive radicles are formed chiefly from the metalloid elements. Finally, the production of strong bases by the addition of quinoline or pyridine to mercuric oxide; the formation of bases, like those of the alkalis, through the addition of ammonia or amines to weakly basic metallic hydroxides; and lastly, the fact that triphenylmethyl carbinol, although containing three negative phenyl residues, is a much stronger anhydrobase than alcohol, etc., are phenomena which are to be reviewed from the same standpoint.

(b) The Theory of Acids.

1. Definition of an Acid.

At the present time acids are defined as compounds with hydrogen which, on solution in water, dissociate, giving hydrion. A critical examination of the behaviour of such hydrogen compounds leads to the result, that the definition does not describe what takes place on their solution. This statement is based upon the following reflections.

Acids are characterized by the fact that their hydrogen atoms

are able to form salt-like addition-compounds with very different kinds of molecules. Such addition-reactions are, for example, the following:

$$XH + NH_3 = XH \cdot NH_3$$

 $XH + O = XH \cdot O = XH \cdot O = Me$

Additions similar to those in which ammonia, amines, and metallic hydroxides take part are also taken part in by alcohols. Thus, McIntosh was able to isolate the following addition-compounds at low temperatures from alcoholic solution:

It is therefore to be expected that, in aqueous solution, acids will also combine with those radicles of water which are able to form such addition-compounds. Of such radicles water yields two, viz. the molecule itself and hydroxylion. Consequently, there are to be expected oxonium salts:

$$\mathbf{H}_2\mathbf{O} + \mathbf{H}\mathbf{X} = \mathbf{H}_2\mathbf{O} \cdot \mathbf{H}\mathbf{X}$$

and addition-products with hydroxylion:

$$\dot{H} + \bar{O}H + HX = \dot{H} + H\bar{O} \cdot HX$$

The latter reaction can be imagined as taking place through the dissociation of the hydrate;

$$XH \cdot OH_2 \rightarrow XH \cdot OH + H$$

This discussion shows that hydrion in the aqueous solutions of acids, such as HCl, HBr, etc., is not produced by the dissolution of hydrogen from the acid, but rather comes directly from the water, and consequently water plays the chief part when hydrogen compounds act as acids.

In agreement with this statement is the fact that these hydrogen compounds in other solvents, e.g. HCl in trichloracetic acid, do not form hydrogen ions.

Such addition-compounds as those just discussed are obviously only special types of the addition-compounds which already have

¹ J. Amer. Chem. Soc., 27, 1013 (1905).

received full treatment. The metallic atom in the metallic salts is able to play an exactly analogous part to hydrogen in the acids. The compounds of tetravalent platinum afford an illustration of this behaviour. Plate hydroxide and plate chloride form addition-compounds with water corresponding to the following equations:

$$(HO)_4Pt + 2H_2O = (HO)_4Pt(OH_2)_2$$

 $Cl_4Pt + 2H_2O = Cl_4Pt(OH_2)_2$

which in conformity with the ionic theory may be written:

$$(HO)_{4}Pt + 2\overset{+}{H} + 2\overset{-}{O}H = (HO)_{4}Pt(\overset{-}{O}H)_{2} + 2\overset{+}{H}$$
and
$$Cl_{4}Pt + 2\overset{+}{H} + 2\overset{-}{O}H = Cl_{4}Pt(\overset{-}{O}H)_{2} + 2\overset{+}{H}$$

From this it follows that HCl, HBr, etc., are not analogous to $\text{Cl}_4\text{Pt}(\text{OH}_2)_2$ but rather to PtCl_4 , *i.e.* they are, just like the latter, to be considered as acid anhydrides. Since under the term "acid anhydride" a definite kind of oxide is understood, in what follows, and in keeping with the term "anhydro-base" compounds such as XH, $\text{Pt}(\text{OH})_4$, PtCl_4 , etc., will be called "anhydro-acids."

The following definitions describe the conception of an acid:

- 1. A difference must be made between anhydro-acids and aquo-acids.
- 2. Every compound which with water forms a hydrate, which is dissociated in aqueous solution into hydrions, is an anhydro-acid.
- 3. Every addition-compound formed with water, which in aqueous solution dissociates into hydrion, is an aquo-acid, or shortly, an acid.

Anhydro-acids may, in keeping with the electro-chemical theory, be defined as follows:

4. Compounds which in aqueous solution combine with the hydroxyl ions of water, and in this way disturb the dissociation equilibrium of water until a value is reached which is characteristic for that compound, are anhydro-acids.

2. Sub-divisions of Anhydro-acids.

According to the nature of the element which combines with the oxygen of the water molecule is it possible to sub-divide anhydro-acids.

In the first great group are the hydrogen acids, i.e. the compounds of hydrogen in which the latter has the property, in the sense of the following equations, of combining either with water or hydroxyl:

$$XH + OH2 = XH \cdot OH2$$

$$XH + HO + H = XHOH + H$$

To this group belong the halogen acids and also a great number of the oxygen acids, like nitric acid, perchloric acid, etc., the hydrates of which can be isolated under suitable conditions.

Many of the so-called oxygen acids are certainly to be classed as anhydro-acids. The following arguments support this statement. The hydrogen of nitric acid has the property of forming an addition compound with ammonia, and hence in aqueous solution hydroxl ions will also combine with the hydrogen atom:

$$NO_3H + H\bar{O} + \dot{H} = NO_3H \cdot \bar{O}H + \dot{H}$$

and in this way the concentration of hydrion in solution increases, and this reaction, on account of the unsaturated character of the hydroxyl ions, will always predominate in solution. Other oxygen compounds will form acids which set up an equilibrium with their free forms or with derivatives poorer in water. Thus, carbonic acid, sulphur acid, etc., illustrate such a case, for their derivatives poorer in water, i.e. CO₂, SO₂, etc., combine with hydroxl ions, and thus act as anhydro-acids:

$$O_2C + H\bar{O} + \dot{H} \gtrsim O_2C \cdot \bar{O}H + \dot{H}$$

 $O_2S + H\bar{O} + \dot{H} \gtrsim O_2S \cdot \bar{O}H + \dot{H}$

From this standpoint it is possible to determine which compound acts as the anhydro-acid.

To the class of anhydro-acids also belong such metallic hydroxides as Zn(OH)₂, Al(OH)₃, Pt(OH)₄, Pb(OH)₄, Sn(OH)₄, and we have consequently zinc anhydro-acids, aluminium anhydro-acids, etc.

Finally, it may be stated that the most diverse elements yield compounds which are able to combine with hydroxylion, and hence such compounds exercise the characteristic function of anhydroacids.

3. On the Behaviour of Aquo-acids on Salt Formation

In the aqueous solutions of hydroxide bases and hydrogen acids we assume the presence of aquo-bases and aquo-acids, which can be expressed by the following formulæ:

$$\begin{bmatrix} \mathbf{R} \\ \mathbf{H} \end{bmatrix}$$
 $\mathbf{O} \cdot \mathbf{H} \end{bmatrix}^{\dagger} + \bar{\mathbf{O}}\mathbf{H} \quad \text{and} \quad (\mathbf{X}\mathbf{H} \cdot \bar{\mathbf{O}}\mathbf{H}) + \bar{\mathbf{H}}$

When such solutions are mixed, the hydroxyl and hydrogen ions form water:

$$\begin{bmatrix} \mathbf{R} \\ \mathbf{H} \end{bmatrix} = \mathbf{\bar{O}} \cdot \mathbf{\dot{H}} + \mathbf{\bar{O}} \mathbf{H} + (\mathbf{X} \mathbf{H} \cdot \mathbf{O} \mathbf{\dot{H}}) + \mathbf{\dot{H}} = \mathbf{H}_{2}\mathbf{O} + \begin{bmatrix} \mathbf{R} \\ \mathbf{H} \end{bmatrix} = \mathbf{O} \cdot \mathbf{\dot{H}} + (\mathbf{X} \mathbf{H} \cdot \mathbf{O} \mathbf{\dot{H}})$$

and the equation shows that in hydrated ions R.OH₂ and X.H₂O are still present. In this way we come to the same conclusion which, on other grounds, has also been attained, viz. the ions of dissociated salts combine with the solvent to form complex ions. It depends upon the nature of the base and acid whether the salt on crystallization crystallizes with or without some of the solvent. This has already been made clear when discussing the bases.

(c) On Amphoteric Compounds.

There are some chemical compounds which are able to take up hydrion and hydroxylion. Such compounds will, when the capacity for taking up either of these ions does not predominate in either direction, display in solution neither strongly basic nor strongly acidic characteristics. When dissolved in acidic solutions, i.e. solutions in which the concentration of hydrion is considerable, then they will take up hydrion and behave consequently as anhydrobases. On the other hand, should they be dissolved in alkaline solutions, i.e. solutions in which the concentration of hydroxylion is great, then they will take up hydroxylion, thus behaving as anhydro-acids. Typical examples of this type are zinc hydroxide and aluminium hydroxide. In acid solution aquo-salts are formed according to the general equation:

$$MeOH + HX = (MeOH_2)X$$

and in alkaline solution hydroxo-salts are formed thus:

$$MeOH + O_K^H = \left[Me \right]_{OH}^{OH} K$$

Compounds which can react according to both these equations are called amphoteric compounds. Amphoteric compounds are not those which can yield on dissociation both hydrion and hydroxylion, but rather those which can take up both hydrion and hydroxylion. Pfeiffer has already drawn attention to this definition, which is a logical consequence of the new theory of bases and acids,

(d) The Theory of Hydrolysis.

At the present time, hydrolysis is supposed to be a chemical decomposition which takes place according to the following equation:

$$\dot{\mathbf{M}}\mathbf{e} + \ddot{\mathbf{X}} + \dot{\mathbf{H}} + \ddot{\mathbf{O}}\mathbf{H} = \mathbf{M}\mathbf{e}\mathbf{O}\mathbf{H} + \dot{\mathbf{H}} + \ddot{\mathbf{X}}$$

the final equilibrium being dependent on the degree of dissociation of the resulting products.

This conception of hydrolysis is inadequate to explain a number of phenomena which have been observed amongst the aquometallic ammino-complexes, and which are certainly to be referred to hydrolytic changes. In order to make this clear let us consider the following hydrolytic change in the aquometallic ammino-salts.

There exist a series of hydroxopentammincobalti salts 1:

$$\left[\mathrm{Co_{(NH_3)_5}^{OH}}\right]\!\mathrm{X}_2$$

which can be brought into genetic relations with three other series of cobalt ammino-complexes, viz. the aquopentammincobalti salts:

$$\left[\mathrm{Co_{(NH_3)_5}^{OH_2}}\right]\!X_3$$

the acidopentammincobalti salts:

$$\left[{^{\mathrm{Co}}_{(\mathrm{NH_3})_5}^{\mathrm{X}}} \right] \! \mathrm{X}_2$$

and the hexammincobalti salts:

How this can be done will be explained by taking the chlorides of these series as examples.

On the addition of hydrochloric acid to hydroxopentammin cobalt chloride aquopentammin cobalt chloride is obtained:

$$\left[{\rm Co_{(NH_3)_5}^{OH}} \right] \! {\rm Cl_2} + {\rm HCl} = \! \left[{\rm Co_{(NH_3)_5}^{OH_2}} \right] \! {\rm Cl_3}$$

On heating the aquochloride or heating a solution and treating it with hydrochloric acid, the molecule of water may be withdrawn and chloropentammin cobalt chloride results:

$$\left[Co_{(NH_3)_5}^{OH_2}\right]Cl_3 = H_2O + \left[Co_{(NH_3)_5}^{Cl}\right]Cl_2$$

Werner, ibid., 40, 4098 (4907).

This last compound, on being treated with concentrated ammonia, is transformed into the hexammin chloride:

$$\left[Co_{(NH_3)_5}^{Cl}\right]Cl_2 + NH_3 = \left[Co(NH_3)_6\right]Cl_3$$

On comparing the chlorides of these four series of salts with respect to their behaviour towards litmus, the following differences become clear:

$$\begin{bmatrix} \text{Co}_{(\text{NH}_3)_5}^{\text{OH}} \end{bmatrix} \text{Cl}_2, \quad \begin{bmatrix} \text{Co}_{(\text{NH}_3)_5}^{\text{OH}_2} \end{bmatrix} \text{Cl}_3, \quad \begin{bmatrix} \text{Co}_{(\text{NH}_3)_5}^{\text{Cl}} \end{bmatrix} \text{Cl}_2, \quad \begin{bmatrix} \text{Co}_{(\text{NH}_3)_6}^{\text{Cl}} \end{bmatrix} \text{Cl}_3$$
Basic Acid Neutral Neutral

From the fact that only the aquochloride reacts acid, i.e. that of the four chlorides only that which contains water is hydrolyzed, it must be concluded that the water molecule in aquopentammin chloride is specially connected with the hydrolysis.

Since the action of ammonia on aquopentammin chloride results in the production of hydroxopentammin chloride, and in consequence of the hydrolysis the hydrochloric acid which is produced is transformed into ammonium chloride, it follows that the only possible way of formulating this change is by the equation:

$$\left[Co_{(\mathbf{NH}_3)_5}^{\mathbf{OH}_2}\right]Cl_3 \ \ \rightleftarrows \ \ \left[Co_{(\mathbf{NH}_3)_5}^{\mathbf{OH}}\right]Cl_2 + \mathbf{H}Cl$$

Accordingly the hydrolysis is due to the decomposition of the aquochloride into hydroxochloride and hydrochloric acid, while according to the customary theory of hydrolysis the compound

$$\left[\mathrm{Co_{(NH_3)_5}^{OH_2}} \right]_{\mathrm{Cl_2}}^{\mathrm{OH}}$$

should have been produced, in which the hydroxyl group should be less dissociated than water. Consequently in the aqueous solution of aquopentammincobalt chloride it should be produced according to the equation:

$$\left[Co_{(NH_3)_5}^{OH_2}\right]Cl_3 + \dot{H} + \bar{O}H = \left[Co_{(NH_3)_5}^{OH_2}\right]_{Cl_2}^{OH} + \dot{H} + \bar{C}l$$

However, against this assumption we must call to mind what has been pointed out already, i.e. such a compound containing an indirectly bound hydroxyl group should be very strongly electrolytically dissociated.

But, in order to explain this contradiction, it might be suggested

that the aquo-base, in its turn, gives up water and thus passes into the hydroxo-compound:

$$\left[C_0^{\text{OH}_2}_{(\text{NH}_3)_5}\right]_{\text{Cl}_2}^{\text{OH}} = \left[C_0^{\text{OH}}_{(\text{NH}_3)_5}\right]_{\text{Cl}_2} + H_2O$$

Such an hypothesis can be shown experimentally to be incorrect. For if the aquo-base is the primary product of the action of water, then its production can be prevented by decreasing the concentration of the hydroxyl ions. A strongly acid solution of the hydroxo-salt, therefore, should only contain the aquo-salt, for in such a solution it would be very improbable that sufficient hydroxyl ions were still present to bring about the hydrolysis of the aquo-salt into aquo-base and free acid. As a matter of fact, it is possible, on adding neutral salts, to precipitate the hydroxo-salt unchanged from its solution in concentrated acetic acid, although these salts yield weakly alkaline aqueous solutions.

The following salts illustrate these changes.

Most hydroxoaquodiethylenediammincobalti salts,

$$\left[en_2Co_{OH_2}^{OH}\right]X_2$$

are fairly insoluble in water, but on adding acetic acid, they dissolve, colouring the solution the colour of the diaquo-salts. It is, therefore, to be assumed that the acetic acid forms a salt, thus

From these acetic acid solutions the addition of metallic salts reprecipitates the hydroxo-salts in an unchanged condition. All this series of salts are weakly basic towards litmus.

Another series of salts 2 are known, i.e. the following:

$$\begin{bmatrix}\mathbf{HO}\\\mathbf{H_2O}\mathbf{Co_{(NH_3)_2}^{Py_2}}\end{bmatrix}\mathbf{X_2}$$

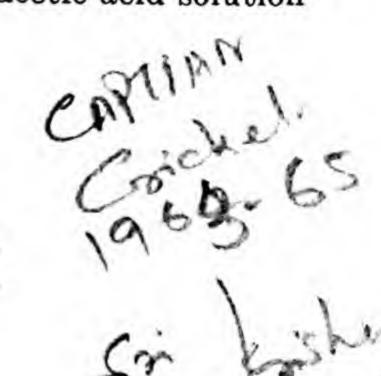
which are even precipitated from a 50-per-cent. acetic acid solution on the addition of metallic salts.

Again, the behaviour of the chloride,

$$\begin{bmatrix} \mathbf{P}\mathbf{y_2} \\ (\mathbf{H_3}\mathbf{N})_2 \mathbf{Co}(\mathbf{OH_2})_2 \end{bmatrix} \mathbf{Cl_3}^2$$

Werner, Ber., 40, 272 (1907).

Werner, ibid., 40, 468 (1907).



which yields strongly acid solutions, is of considerable interest. Sodium dithionate and sodium nitrate precipitate the corresponding diaquo-salts:

$$\begin{bmatrix} Py_2 \\ (NH_3)_2 Co_{OH_2}^{OH_2} \end{bmatrix}_2 (S_2O_6)_3 \quad and \quad \begin{bmatrix} Py_2 \\ (H_3N)_2 Co_{OH_2}^{OH_2} \end{bmatrix} (NO_3)_3$$

but potassium bromide precipitates the hydroxo-bromide:

$$\begin{bmatrix} \mathrm{Py_2} \\ (\mathrm{H_3N})_2 \mathrm{Co}_{\mathrm{OH_2}}^{\mathrm{OH}} \end{bmatrix} \mathrm{Br_2}$$

which is a weakly alkaline salt.

Still more peculiar is the fact that the addition of hydrobromic acid to the aqueous solution of the corresponding diaquobromide precipitates the hydroxoaquobromide.

Obviously, then, the supposition that the hydroxyl ions of water influence, in the above cases, the formation of hydroxo salts is without foundation. Consequently the conclusion is forced upon us that the theory of hydrolysis proposed by Arrhenius is insufficient to explain the facts.

A very simple theory of hydrolysis, explaining all the facts which have been encountered during the study of the aquometallic and hydroxometallic ammino-complexes, can be formulated from the following considerations.

Hydrolytic changes are such as may be represented by the general equation:

$$R.HX \geq R+HX$$

They are dissociations similar to those observed in the presence of water, e.g. the dissociation of the vapour of ammonium chloride. The degree of the hydrolysis, therefore, must primarily be dependent upon the stability of the water in group R. Since, in keeping with the ionic theory, the above equation may be written

$$R.\dot{H} + \bar{X} \geq R + \dot{H} + \bar{X}$$

and thence in aqueous solution the chief rôle is played, not by the hydrogen of XH as such, but rather by the much more active hydrogen ions, therefore hydrolysis depends chiefly upon the degree of strength with which hydrion is linked in R; in other words, it depends upon the tendency of hydrion to form complexes with R. Again, since the equation is an equilibrium equation, it follows that the degree of hydrolysis will be determined by the

concentration of the RH and H ions. In opposition to the theory of Arrhenius, the present theory does not attribute hydrolysis to the hydroxyl ions of water.

A special case of hydrolysis is that in which R is a metallic hydroxide.

In this case the general equation takes the form:

$$Me$$
 $O \cdot \mathbf{H} + \overline{\mathbf{X}} \geq Me$
 $O \cdot \mathbf{H} + \overline{\mathbf{X}}$

And we again have the reaction describing the hydrolysis of the metallic ammino-compounds, which served as the starting-point for the revision of the theory of hydrolysis.

Pfeiffer 1 has shown that the application of the law of mass action to the above general equation leads to the same mathematical expression for the quantitative relations between the hydrolysis of the metallic salts, the dissociation of water, and the strength of metallic base as the theory of Arrhenius. Consequently we arrive at the result that this equation offers a more satisfactory quantitative explanation of hydrolysis than that of Arrhenius.

(a) Definition of an Inner Metallic Complex Salt.

When discussing addition-compounds only those were considered in which the groups were separately attached, either by principal or auxiliary valencies, to the central metallic atom, i.e. they were not combined with one another. But it may so happen that all these groups may be joined up to one another. An example will make this clear. Copper acetate has the property of forming an addition-compound with two molecules of ammonia, thus:

Since in amidoacetic acid (glycocoll) acetic acid and ammonia are combined together without seriously affecting the functions of either, it is quite to be expected that they will form an analogous copper derivative of the following formula:

¹ Ber., 40, 4036 (1907).

² Schiff, Annalen, 123, 43 (1862),

The work of Bruni 1 and Ley 2 has shown that this is correct. Salts like this, in which the metallic atom is linked up by both principal and auxiliary valencies, are called, after Ley's suggestion, inner metallic complex salts. Although their nature has been recognized only quite recently, yet they have attained, in many directions, to considerable importance.

(b) Review of the Inner Metallic Complex Salts.

The first inner metallic complexes were discovered by the author when examining the acetylacetone compounds of platinum. When acting on potassium platinous chloride with acetylacetone, it was found that a molecule of potassium chloride and an atom of chlorine are replaced by one molecule of acetylacetone:

$$\frac{\mathrm{KCl}_{\mathrm{Cl}}\mathrm{Pt}_{\mathrm{ClK}}^{\mathrm{Cl}} + \sum_{\mathrm{O}=\mathrm{C}}^{\mathrm{KO}-\mathrm{C}}\mathrm{CH}_{3}}{\mathrm{CH}} = 2\mathrm{KCl} + \sum_{\mathrm{Cl}}^{\mathrm{KCl}}\mathrm{Pt}_{\mathrm{O}=\mathrm{C}}^{\mathrm{C}}\mathrm{CH}_{3}$$

Dilthey,³ with some pupils, examined the β -diketo-compounds of silicon and boron, and found that each β -diketo residue:

always occupied two co-ordination positions. Consequently, all six co-ordination positions of silica and all four of boron would be occupied respectively by three and by two β -diketo residues. But since in each of the resulting compounds, $(SiAc_3)X$ and $(BAc_2)X$, a valency of the central atom takes up an acid residue X, it follows that the saturation of this latter valency does not take place in the first but in the second zone, *i.e.* the acid residue must be indirectly attached to the central atom.

² Ley, Zeitsch. Electrochem., 10, 954 (1904).

¹ Bruni and Fornaro, Atti R. Accad. dei Lincei, Roma, (5) 13, II. 26 (1904).

³ Ber., 38, 569 (1905); Annalen, 322, 280 (1902); 344, 300 (1906).

The result of this is that the acid residue must have ionogen properties, as Dilthey, in his classical researches, has shown.

Tschugaeff has prepared, by acting on different metallic ammino-complexes with a-dioximes, salts which are of great importance to the theory of inner complexes. He has shown that these a-dioximes, which can enter the molecule of the metallic ammino-complexes as monovalent groups, always occupy two co-ordination positions. The following compounds result on treating chloropentammin-cobalt chloride and nitropentammincobalt chloride with dimethyl-glyoxime:

$$\mathbf{H_3NCo_{Cl}^{D_2H_2}}$$
 and $\mathbf{H_3NCo_{No_3}^{D_2H_2}}$

(D₂H₂ corresponds to two molecules of dimethyl glyoxime).

Tschugaeff ¹ also was able to prepare the compounds:

$$\left[Co_{D_{2}H_{2}}^{(NH_{3})_{2}} \right] \! X, \quad \left[Co_{D_{2}H_{2}}^{(NH_{2}C_{2}H_{5})_{2}} \right] \! X \quad \text{and} \quad \left[Co_{D_{2}H_{2}}^{Py_{2}} \right] \! X$$

In all these compounds the oxime must be connected to the metallic atom, thus:

The a-dioximes also have the property of forming very stable salts with the heavy and platinum metals. Such salts Tschugaeff has called glyoximines. The plato- and pallado-compounds can be distilled in vacuo without decomposing.

Quite similar complex salts can be prepared from the a-oxime of a-benzoylpyridin 3, and also from nitrosoguanine 3:

The amido-acids have proved to be particularly suited for the study of these inner salts. The researches of Bruni 4 and of Ley 5

¹ Ber., 39, 2692 (1906).

² Zeitsch. anorg. Chem., 46, 144 (1905).

² Ber., 39, 3382 (1906).

¹ Chem. Zentr., 1904, p. 824.

⁵ Zeitsch. Elektrochem., 10, 954 (1904); Ley and Krafft, Ber., 40, 697 (1907).

on copper glycocoll have led to the same result, viz. copper glycocol, is an inner complex salt. Ley has given it the following constitution:

The copper salts of diethylaminoacetic acid, piperidoacetic acid, phenylglycocoll, alanine and probably all the copper salts of a-amino acids have the same constitution as copper glycocoll. The same is true of the nickel salts.

Callegari 1 has shown that the copper and nickel salts of hydrazine carbonic acid, H₂NNH—COOH, are inner complex salts.

Ley and Kraft have prepared some inner complex salts of oxyamidines which correspond to the general formula:

$$\begin{array}{c} R \\ R = C = N \\ \downarrow \\ R_2N = O \end{array} Me$$

And Ley² has also found that the azohydroxyamides, the oxyamidoximes, and the oxyguanidines form inner complexes.

The copper and nickel salts of biuret and analogous compounds form a very interesting group,³ for copper biuret has a constitution which is similar to the copper and nickel salts of dicyandiamidine and of biguanide.⁴

Finally, Tschugaeff ⁵ has shown that the α-isonitrosoketones are able to form inner complex salts.

This short review clearly shows that this class of complex salts already has attained considerable proportions, and in this class are also to be included most adjective dyes.

(c) Properties of Inner Complex Salts.

1. Anomalous Behaviour with reference to Electrolytic Dissociation and Analytical Reactions.

The peculiar constitution of inner complex salts prevents the metal, when the auxiliary valency compound is stable, from appearing

¹ Gazz. chim., 36, 63 (1906).

² Ber., 40, 697 (1907).

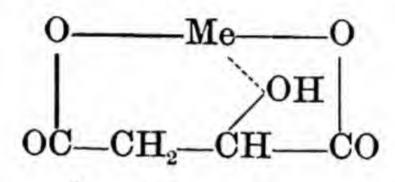
³ Ley and Werner, ibid., p. 705.

¹ Tschugaeff, ibid., p. 1974.

⁵ J. pr. Chem., (2) 75, 153 (1907); (2) 76, 88 (1907).

as an ion in solutions. This results in such complexes exhibiting in solution a normal molecular weight and a very trifling conductivity. This has been proved in a way which leaves no room for doubt by the researches of Bruni and Ley. The concentration of the copper ions in these complex salts is extremely small; that of the nickel is a little greater, probably because the auxiliary valencies of nickel are somewhat weaker.

The abnormally small conductivity which Tower 1 obtained for certain salts of malic and tartaric acids is probably due to the formation of such inner complexes. The conductivity of the magnesium, barium, and manganese salts of these acids is normal, but that of the nickel and cobalt salts is abnormally small. The inner complex salts of malic acid will probably correspond to the formula:



Hand in-hand with the abnormally small conductivity of these inner complexes goes an abnormal analytical behaviour; the metals are either incompletely, or not at all, precipitated by the usual reagents from the solutions of these salts. Thus, alkaline hydroxides and sulphuretted hydrogen are unable to precipitate the copper, nickel, and cobalt from their salts with the amino-fatty acids. Further, Zelinsky and Schlesinger 2 have shown that the copper cannot be precipitated by the continuous passing of H₂S or by introducing semi-carbazide into a neutral solution of its salt with aα'-dimethylpyrrholine-α-carbonic acid.

2. The Anomalous Colour of Inner Complex Salts.

The mere inspection of the colour of a metallic salt will often decide whether it is an inner complex salt or an ordinary salt, for most of the former are coloured differently to the latter. Bearing in mind the complicated constitution of inner complex salts, it is not surprising that their colour is greatly influenced by the nature of the groups which are linked together by auxiliary valencies. A good illustration of this is afforded by comparing the colour of anhydrous

¹ J. Amer. Chem. Soc., 24, 1012 (1902). ² Ber., 40, 2887 (1907).

chromium chloride, with some of its co-ordination compounds. Anhydrous chromium chloride is reddish-violet, the addition-compound with six molecules of ammonia is pure yellow, that with five of ammonia and one of water is a yellowish-orange, that with four of ammonia and two of water is brick-red, that with three of ammonia and three of water is red, that with two of ammonia and four of water is bluish-red, and that with six of water is violet-blue. When to this series is added that the compound with six molecules urea is pure green, then it is obvious that the complex compounds of chromium can display all the colours in the spectrum. Exactly the same is true of all other coloured metallic salts.

From this it is clear that the colour of an inner complex salt can be different to that of the ordinary metallic salt, and that the colours vary with the nature of the components.

Two more striking examples of this are worthy of notice.

The ordinary copper salts have a pure blue colour, but the inner complex salts with the a-amido acids are coloured a blue which resembles that of the copper ammino-complexes, and the copper salts of the oxyamidines are brown to brownish-red.

Contrary to the green colour of the simple nickel salts, complex salts of nickel are often yellow and that with dimethylgloxime is a bright red.

3. Solubility of Inner Complex Salts.

It is often observed that inner complex salts are only soluble with difficulty; this is true of the salts of the glyoximes, the a-isonitrosoketones, etc.

This insolubility has given rise to many new methods for the quantitative estimation of metals, Tschugaeff suggested the use of dimethyl glyoxime for the estimation of nickel and Grossman dicyandiamide;

$$HN = C \begin{cases} NH_2 \\ NH-CN \end{cases}$$

for the same purpose. Cobalt has long been estimated by using nitroso- β -naphthol.

Since the metals often exhibit a surprising tendency for the formation of inner complexes, it is to be expected that continued research on this type of compound will reveal many compounds of value to analytical chemistry.

(d) Dependence of the Formation of Inner Complexes on the Constitutions of the Components.

The formation of inner complex salts is characterized by the formation of a ring. The study of these ring-compounds has shown that they are controlled by exactly the same laws which control the formation of principal valency rings.

Inner complex salts have, up to the present, been found only to consist of five or six members, and the latter are very often unstable. Thus, a-amido-fatty acids form well-characterized inner complex salts, but Callegari has shown that the β -amido acids are unable to do so, for the copper salt of β -amidopropionic acid has no abnormal properties. The same is true of the copper and nickel salts of amidosulphonic acid:

 $(NH_2SO_3)_2Cu + 2H_2O$ and $(NH_2SO_3)_2Ni + 4H_2O$

which exhibit normal properties. On the other hand, the nickel salt of hydrazinecarbonic acid (NH₂. NHCOO)₂Ni forms an inner complex, for it is blue in colour and does not give the usual reactions of nickel.

(e) Signification of Inner Complex Salts for Adjective Dyes.

The author has been able to prove that those compounds which are able to form inner complex salts are also able to colour mordanted stuffs.² This is true of the β -diketones, the α -isonitrosoketones, the α -diketoximes, the amidoximes, and the hydroxam acids. And all the laws on the constitution of adjective dyes conform with those under which inner metallic complex salts are formed. Consequently adjective dyes, or at any rate the great majority of this class of compounds, may be defined as compounds which under suitable conditions are able to form inner metallic complex salts.

11. On Complexes containing a Negative Central Atom.

The great majority of complex compounds contain a positive central atom, but there exists a small group of compounds which contain a negative central atom. This group has lately received considerable attention.

¹ Gazz. chim., 86, II. 63 (1906).

² Werner, Ber., 41, 1062 (1908).

Hellwig¹ has investigated the product resulting from the addition of silver nitrate to silver iodide, i.e. AgI + 2AgNO₃, and has shown that it contains the complex radicle (IAg₃), and hence has the following constitution:

$$\begin{bmatrix} \cdot & Ag \\ I \cdot Ag \\ \cdot & Ag \end{bmatrix} (NO_3)_2^2$$

A salt corresponding to the formula (IAg₂)NO₃ also exists, and it has been shown ³ that (IAg₂) is the complex cation.

It is probable that the salts AgBr + AgNO₃, AgCN + AgNO₃, and AgSCN + 2AgNO₃⁴ contain the complex cations, (Ag₂Br), (Ag₂CN) and (Ag₃SCN). Further, the compounds Ag₃P. 3AgNO₃⁵ and Ag₃As. 3AgNO₃ are to be considered as salts containing the cations (PAg₆) and (AsAg₆).

A group of compounds in which, in all probability, complex radicles with negative central atoms play a part are the chloromercurates, the highest of which correspond to the formula $RCl(HgCl_2)_6$. The composition and behaviour of these compounds would agree very well with the supposition that a variable number of $HgCl_2$ molecules combine with the chlorine atom, which acts as the central atom. A similar case was investigated by the author, and it was shown that several molecules of platosalts combined with one molecule of a platesalt.

Iodine has a remarkably great tendency for the formation of addition-compounds. This property evinces itself in the addition compounds which iodine chloride forms with amines, e.g. $(H_3C)_3N$. ICl, Py. ICl, Chin. ICl, and Pip. ICl. These compounds behave in a manner which is completely analogous to the addition-complexes formed by the metals, for hydrochloric acid transforms them into halogeno-salts:

$$(CH_3)N \cdot ICl + HCl = (CH_3)_3N \cdot H(ICl_2)$$

¹ Zeitsch. anorg. Chem., 25, 157 (1900).

² Kistiakowski, J. Russ. Phys. Chem. Soc., 33, 592 (1901).

³ Ibid.

⁴ Vitali, L'Orosi, 15, 397.

⁵ Vitali, ibid., 16, 10; Poleck and Thümmel, Ber., 16, 2435 (1883).

⁶ Zeitsch. anorg. Chem., 12, 46 (1896).

¹ Pictet and Krafft, Bull. Soc. Chim., (3) 7, 74 (1892).

To the same group of compounds also belong H_3N . INH_2 and H_3N . INI_2 .¹

Hantzsch and Graf ² showed that bromine also was able to form addition-compounds with amines. The following compounds were prepared by them:

$$(\mathbf{H}_{3}\mathbf{C})_{3}\mathbf{N} \cdot \mathbf{Br}_{2}, \qquad \begin{array}{c} (\mathbf{CH}_{3})_{2}\mathbf{N} \cdot \mathbf{Br}_{2}, & (\mathbf{CH}_{3})_{2}\mathbf{N} \cdot \mathbf{Br}_{2}, \\ \mathbf{C}_{6}\mathbf{H}_{5} & \mathbf{Br}\mathbf{C}_{6}\mathbf{H}_{4}\mathbf{N} \cdot \mathbf{Br}_{2}, \end{array}$$

and from their behaviour these workers concluded that constitutions similar to [(H₃C)₃NBr]Br were to be given to these salts.

Iodine and bromine also take up oxygen compounds. The constitutions of these compounds has been investigated by Hantzsch.⁴ He described the following compounds: Diethoxydinaphthostilbenetetriodide, diethoxydinaphthostilbenedibromide - tetraiodide, dixanthylenetetraiodide, and also higher iodides up to decaiodides. He also was able to show that dimethylpyrone formed a diiodide in ethylene bromide solution.

Bromine yields the following addition-compounds: Diethoxy-dinaphthostilbenetetrabromide, diethoxydinaphthostilbenedibro-mide-tetrabromide, dixanthylenetetrabromide. To this group also belong the following compounds prepared by McIntosh: 5

$$C_2H_5$$
 O. BrBr, C_2H_5 O. BrBr and $[C_4H_8O_2]_2(Br_2)_3$ Ethylacetate

From what has already been said, it will be clear that beginnings have been made in the chemistry of this interesting class of compounds. The class is, however, much more extensive than it at present appears to be, and consequently it will first be necessary to examine within what limits it is possible to prepare such compounds.

12. On the Auxiliary Valency Compounds of the Elements.

In the previous sections compounds belonging to this class have already been met with, e.g. the addition-compounds of organic oxides and nitrides with bromine and iodine. But a large number of auxiliary valency compounds of other elements are also known which, on account of their peculiar composition, deserve special mention.

Raschig, Annalen, 230, 223 (1885).

Ber., 38, 2154 (1905).

Ibid., p. 2161.

Trans., 87, 784 (1905).

The hydrates of bromine and chlorine belong to this class, and since iodine solutions are brown in colour, it is to be assumed that iodine forms an addition-compound with the solvent.

Calcium and barium form the compounds Ca(NH₃)₆ and Ba(NH₃)₄ with ammonia. Ruff and Geikel ¹ have shown that the addition-compounds of the alkali metals with ammonia, Me.NH₃, do not exist, as was once assumed.

The auxiliary valency compounds which iron and nickel form with carbon monoxide are deeply interesting. That carbon monoxide is linked by auxiliary valencies is shown by its behaviour in potassium carbonylferrocyanide and in the carbonyl-compounds of platinum. Nickel tetracarbonyl 2 and iron pentacarbonyl 3 consequently have the following constitutions:

$$\begin{array}{cccc} \mathrm{OC} & . & \mathrm{CO} & & \mathrm{OC} & . & \mathrm{CO} \\ & \mathrm{Ni} & & \mathrm{and} & & \mathrm{Fe} \cdot \mathrm{CO} \\ \mathrm{OC} \cdot & \cdot \mathrm{CO} & & \mathrm{OC} \cdot & \cdot \mathrm{CO} \end{array}$$

13. General Considerations on the Formation of Compounds of the Higher Order.

The nature of those compounds which are able to form addition-compounds undergoes a regular variation in the different elementary groups in the periodic system. Thus, only the inorganic halides are suited to form such compounds, the alkyl- and arylhalides being almost inactive. Only in very isolated instances has it been found possible to form additions with alkylhalides, namely in the following:

 $\begin{array}{l} \label{eq:compounds} \ [C(NO_2)_3]Ag + 2ICH_3 \ and \ analogous \ compounds \ with \ benzyl- \ and \ allyliodide,^4 \\ NO_3Ag \, . \ BrCH_2CN, \quad NO_3Ag \, . \ ICH_2CN, \quad NO_3Ag \, . \ I_2CH_2.^5 \end{array}$

In the oxygen group both organic and inorganic oxides and sulphides exhibit a great capacity for the formation of additioncompounds; this property is much diminished in the inorganic

Ber., 39, 828 (1906).
 Mond, Langer and Quincke, Chem. News., 62, 97 (1890); Berthelot, Compt. rend., 112, 1343 (1891).

Mond and Langer, Chem. News., 64, 294 (1891).
 Hantzsch and Caldwell, Ber., 39, 2474 (1906).

⁵ Scholl and Steinkopf, ibid., p. 4393.

selenides, and has not yet been observed amongst the inorganic tellurides. On the other hand, the organic selenides display it in a very pronounced way.

Finally, in the nitrogen group, with the exception of ammonia, very few inorganic nitrides can form addition compounds; but, on the other hand, innumerable organic nitrides have this property. Passing to phosphorus and arsenic, the tendency towards the formation of organic addition compounds is still greater, for the phosphines and arsines form addition complexes which are completely analogous to the ammino-complexes.

The capacity of the elements to act as nuclei for the formation of complexes is also very variable. But the study of complex salts will have to be much further advanced before this side of the question can receive a satisfactory treatment.

A further question which is of interest in connection with complex salts, is the strength with which the individual components are combined. Determinations of this, naturally, can only be carried out with compounds in which the components are comparatively weakly linked together. For it would be impossible to carry out such determinations with, for example, the majority of the metallic ammino-compounds which, under the most varied conditions, are perfectly stable.

Abegg and Bodländer, with their pupils, have attacked this question. Their results, as well as those obtained by Euler, have made us acquainted with the stability in aqueous solution of a great many complex compounds. At present it is impossible to decide how far Abegg and Bodländer are justified in assuming that the tendency for complex-formation is all the greater the smaller the electro-affinity of the central atom, because too little is known of the other factor which is of importance in the formation of complex salts, i.e. the chemical affinity of the component elements.

III. Isomerism in Inorganic Compounds.

Inorganic compounds, with the exception of the simple bases, acids, and salts, are very complicated, and they are either difficult to prepare synthetically or their mode of formation does not explain

¹ See the references to the literature, Abegg, Ber., 36, 3684 (1903), ² Ber., 36, 3400 (1903).

their constitution. It is, therefore, very fortunate that the existence of well-characterized isomeric phenomena offer a means by which insight into the complicated constitution of these compounds may be obtained.

In the following pages it will be seen that isomerism plays a considerable part in the chemistry of inorganic compounds, and that the number of isomeric phenomena is already great. Further, inorganic isomerism is much more varied than organic isomerism, because it does not proceed from a single cause but from many, and these, in their turn, have not yet been fully cleared up.

These various species of isomerism will be described in the following sections.

1. Polymerization.

(a) Co-ordinative Polymerization.

One group of inorganic polymerides includes compounds which possess the same empirical formula, but their molecules contain different multiples of the primary complex.

The first object to be attained in the examination of these polymerides was the nature of the basic and acidic radicles of which they were composed, and, secondly, their synthesis. In this manner light was thrown upon the structure of such isomeric compounds, which are very numerous in inorganic chemistry.

The constitution of the polymeric metallic ammino-complexes has been thoroughly examined and cleared up. To this group belong nine compounds with the empirical formula: $Co(NH_3)_3(NO_2)_3$. The following is the list of these compounds with their constitutional formulæ appended:

- 1. Simple molecular formula: Co(NH₃)₃(NO₂)₃ / Triammincobalt nitrite ¹: [(H₃N)₃Co(NO₂)₃]
- Double molecular formula: Co₂(NH₃)₆(NO₂)₆
 (a) Hexammincobalti-hexanitrocobaltiate:²

[Co(NH₃)₆]III [Co(NO₂)₆]III

¹ Erdmann, J. pr. Chem., 97, 406 (1866); Gibbs, Proc. Amer. Acad., 1874, p. 14; Jörgensen, Zeitsch. anorg. Chem., 7, 300 (1894); 13, 172 (1897); Werner, ibid., 6, 174 (1894); 15, 166 (1897); Werner and Miolati, Zeitsch. Physikal. Chem., 12, 35 (1893); 21, 227 (1896).

² Jörgensen, Zeitsch, anorg. Chem., 5, 177 (1894).

(b) Dinitrotetrammincobalti-tetranitrodiammincobaltiate:

$$\left[C_0_{({\bf NH_3})_4}^{({\bf NO_2})_2}\right]^I \cdot \left[C_0_{({\bf NO_2})_4}^{({\bf NH_3})_2}\right]^I$$

The compounds exist in two stereoisomers.

3. Triple molecular formula : $Co_3(NH_3)_9(NO_2)_9$ Nitropentammincobalti-tetranitrodiammincobaltiate : 2

$$\left[\text{Co}_{(\text{NH}_3)_3}^{\text{NO}_2} \right]^{\text{II}} \cdot \left[\text{Co}_{(\text{NO}_2)_4}^{(\text{NH}_3)_2} \right]_{2}^{\text{I}}$$

- 4. Quadruple molecular formula: Co₄(NH₃)₁₂(NO₂)₁₂
 - (a) Hexammincobalti-tetranitrodiammincobaltiate: 3

$$\begin{bmatrix} \text{Co}(\text{NH}_3)_6 \end{bmatrix}^{\text{III}} \cdot \begin{bmatrix} \text{Co}(\text{NH}_3)_2 \\ \text{NO}_2)_4 \end{bmatrix}_3^{\text{I}}$$

(b) 1, 2- and 1, 6-Dinitrotetrammincobalti-hexanitrocobaltiate: 4

$$\left[C_0(NO_2)_2\atop(NH_3)_4\right]_3^1$$
 $\left[C_0(NO_2)_6\right]^{111}$

5. Quintuple molecular formula: Co₅(NH₃)₁₅(NO₂)₁₅ Nitropentammincobalti-hexanitrocobaltiate: ⁵

$$\left[\mathbf{Co_{(\mathbf{NH_3})_5}^{\mathbf{NO_2}}}\right]_3^{\mathbf{II}} \cdot \left[\mathbf{Co(\mathbf{NO_2})_6}\right]_2^{\mathbf{III}}$$

The structure of these compounds has been determined both analytically and synthetically. It has thus been shown that the complex radicles play in these compounds exactly the same part as elementary atoms in simple salts, and therefore it has been possible to determine the constitution of compounds of very high molecular weight.

A similar series of polymerides has been prepared by the author

¹ Ibid., 5, 182 [Croceo and Flavo], 190 (1894); 7, 287 (1894); 13, 183 (1897); Werner and Miolati, ibid., 14, 514 (1894).

² Jörgensen, loc. cit., Werner and Miolati, loc. cit.

Jörgensen, loc. cit., Werner and Miolati, loc. cit.

Jörgensen, Zeitsch. anorg. Chem., 5, 178 (1894) [Croceo]; Werner and Miolati, ibid., 14, 514 (1894) [Croceo]; Jörgensen, loc. cit. [Flavo + 2H₂O]; Werner and Miolati, loc. cit. [Flavo + 2H₂O].

Jörgensen, loc. cit.

from the thiocyanides of chromium. They have the following formulæ:

- 1. Simple molecular formula: $Cr(NH_3)_3(SCN)_3$ Trithiocyanatotriamminchromium 1: $[(H_3N)_3Cr(SCN)_3]$
- 2. Double molecular formula: Cr₂(NH₃)₆(SCN)₆
 - (a) Hexamminchromi-hexathiocyanatochromiate:2

(b) Dithiocyanatotetramminchromi-diammintetrathio

cyanatochromiate:
$$\left[\operatorname{Cr}_{(\operatorname{NH}_3)_4}^{(\operatorname{SCN})_2}\right]^{\operatorname{I}} \cdot \left[\operatorname{Cr}_{(\operatorname{SCN})_4}^{(\operatorname{NH}_3)_2}\right]^{\operatorname{I}}$$

3. Triple molecular formula: $Cr_3(NH_3)_9(SCN)_9$ Thiocyanatopentamminchromi-diamminetetrathiocyanato

chromiate:
$$\left[\operatorname{Cr_{(NH_3)_5}^{SCN}}\right]^{II} \cdot \left[\operatorname{Cr_{(SCN)_4}^{(NH_3)_2}}\right]_2^{I}$$

- 4. Quadruple molecular formula: Cr₄(NH₃)₁₂(SCN)₁₂
 - (a) Hexamminchromi-diammintetrathiocyanatochromiate:2

$$\begin{bmatrix} \mathbf{Cr}(\mathbf{NH}_3)_6 \end{bmatrix}^{\mathbf{III}} \cdot \begin{bmatrix} \mathbf{Cr}(\mathbf{NH}_3)_2 \\ \mathbf{SCN})_4 \end{bmatrix}_3^{\mathbf{I}}$$

(b) Dithiocyanatotetramminchromi-hexathiocyanatochromiate: 3

$$\left[\operatorname{Cr}^{(\operatorname{SCN})_2}_{(\operatorname{NH}_3)_4}\right]_3^{\operatorname{I}} \cdot \left[\operatorname{Cr}(\operatorname{SCN})_6\right]^{\operatorname{III}}$$

5. Quintuple molecular formula: $Cr_3(NH_3)_{15}(SCN)_{15}$ Thiocyanatopentamminchromi-hexathiocyanatochromiate: 4

$$\left[\operatorname{Cr}_{(\mathbf{NH}_3)_5}^{\mathbf{SCN}}\right]_{3}^{\mathbf{II}} \cdot \left[\operatorname{Cr}(\mathbf{SCN})_{6}\right]_{2}^{\mathbf{III}}$$

Pfeiffer 5 has described the co-ordination polymerides:

[Cr en₃][Cr(SCN)₆] and [Cr
$$_{\text{en}_2}^{(\text{SCN})_2}$$
]₃[Cr(SCN)₆] cis- and trans- forms

- Werner and Jovanovits. Not yet published.
- ² Werner and Jovanovits. Not yet published.
- ³ Christensen, J. pr. Chem., 45, 371 (1848).
- 4 Werner and Jovanovits. Not yet published.
- ⁵ Annalen, 346, 28 (1906).

The platinum ammino-complexes yield similar polymeric pounds.

The following polymerides, corresponding to the empirical formula Pt(NH₃)₂Cl₂, are known:

- 1. Simple molecular formula: Pt(NH₃)₂Cl₂ Platosammin chloride 1 and platosemidiammin chloride 2 (stereoisomers): [(H₃N)₂PtCl₂]
- 2. Double molecular formula: Pt₂(NH₃)₄Cl₄ Tetramminplato-chloroplatoate 3: [Pt(NH3),]. [PtCl,]
- 3. Triple molecular formula: Pt₃(NH₃)₆Cl₆ Tetramminplato-ammintrichloroplatoate 4:

$$\left[\operatorname{Pt}(\mathbf{NH_3})_{4}\right]^{II} \cdot \left[\operatorname{Pt}^{\mathbf{NH_3}}_{\mathbf{Cl_3}}\right]_{2}^{I}$$

Polymerides also exist corresponding to the following empirical formulæ: Pt(NH₃)₂(CN)₂ and Pt(NH₃)₂(SCN)₂:

(H₃N)₂Pt(CN)₂ and [Pt(NH₃)₄]. [PtCN₄] Dicyanodiammin platinum 5 Tetramminplatin-tetracyanoplatoate 6 (Monomolecular) (Dimolecular)

 $(H_3N)_2Pt(SCN)_2$ [Pt(NH₃)₄] [Pt(SCN)₄] and Dithiocyanatodiammin platinum 7 Tetramminplato-tetrathiocyanato-(Monomolecular) platoate 8 (Dimolecular)

The following compounds of tetravalent platinum, corresponding to the general formula Pt(NH3)2Cl4, are also known:

- 1. Simple molecular formula: Pt(NH3)2Cl4 Tetrachlorocisdiammin platinum and tetrachlorotransdiammin platinum 10: [(H3N)2PtCl4].
- ¹ Peyrone, Annalen, 51, 1 (1844); 55, 205 (1845); 61, 178 (1847); Odling, Ber., 3, 682 (1870).

² Peyrone, loc. cit.; Cleve, K. Sv. Vet. Akab. Handl., 10, No. 93.

3 Magnus, Pogg. Ann., 14, 242 (1828); Claus, Annalen, 107, 35 (1858); Cleve, loc. cit.

Cossa, Ber., 23, 2503 (1890).

⁵ Buckton, Annalen, 78, 328 (1851).

⁶ Buckton, ibid.; Thann, ibid., 107, 320 (1858).

⁷ Buckton, ibid., 92, 287 (1854).

Buckton, ibid.

⁹ Cleve, loc. cit.; Jörgensen, J. pr. Chem., (2) 16, 356 (1877).

10 Gerhardt, Compt. rend., 1850, p. 273; Annalen, 76, 307 (1850)

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Double molecular formula: Pt₂(NH₃)₄Cl₈
 Dichlorotetrammin platinum-chloroplateate¹:

Also those corresponding to the formula PtPy2Cl4.3

- Simple molecular formula: PtPy₂Cl₄
 Tetrachlorocisdipyridine platinum and tetrachlorotransdi pyridine platinum: [Cl₄PtPy₂].
- Double molecular formula: Pt₂Py₄Cl₈
 Dichlorotetrapyridine-chloroplateate: [Cl₂PtPy₄] [PtCl₆].
- 3. Triple molecular formula: Pt₃Py₆Cl₁₂
 Dichlorotetrapyridine-pyridinepentachloroplateate:

$$[\operatorname{Cl_2PtPy_4}]\left[\operatorname{Pt}^{\operatorname{Py}}_{\operatorname{Cl_5}}\right]$$

Two rhodium polymerides have been prepared which, according to their behaviour and synthesis, have the following constitution:

Wagner ³ has described a very simple case of polymerization. Monomolecular silver cyanide is precipitated by sulphuric acid from potassium silver cyanide. The dimolecular form, probably having the constitution [Ag(CN)₂]Ag, is precipitated by silver nitrate from potassium silver cyanide, thus:

$$[Ag(CN)2]K + AgNO3 = [Ag(CN)2]Ag + KNO3$$

Hydrates also have been shown lately to exhibit this type of isomerism.

Huber and the author 4 have prepared the compound:

$$[Cr(OH_2)_6]_{SO_4}^{SO_4} \cdot [(H_2O)_4CrCl_2] + 2H_2O$$

¹ Cleve, loc. cit.; Gerhardt, loc. cit.

² Jörgensen, Zeitsch. anorg. Chem., 25, 365 (1900).

³ Chem. Zeit., 1902, p. 942.

⁴ Ber., 39, 329 (1906).

which is polymeric with Recouras sulphate, which latter compound, according to Bjerrum, has the constitution:

$$\left[\mathrm{Cr_{(OH_2)_5}^{Cl}}\right]$$
SO₄ + H₂O

Together with Dr. Costachescu¹ the author has prepared two fluorides of chromium to which the formulæ $Cr_{(OH_2)_3}^{\mathbf{F}_3}$ and (CrF_6) [$Cr(OH_2)_6$] are given.

(b) Polymeric Phenomena of Other Descriptions.

Hantzsch and Holl² have described an interesting case of polymerization between the compounds, sulphamide and ammonium sulphimide, which Traube was the first to examine. Sulphamide is monomolecular, and corresponds to formula I.; sulphimide is trimolecular, (O₂SNH)₃, and its ammonium salt corresponds to formula II.:

The metaphosphates are a group of very interesting polymerides. Tammann, in particular, has investigated these compounds, but he has not yet been able to provide them with satisfactory constitutional formulæ. He examined the following groups 3:

- 1. [NaPO₃]₂, Fleitmann and Henneberg's trimetaphosphate.
- 2. [NaPO₃]₃, Fleitmann's dimetaphosphate.
- 3. [NaPO₃]₆, Hexametaphosphate, which contains only two metallic ions, so that the corresponding salts have the following composition:

¹ Ber., 41, 4242 (1908).

² Ber., 34, 3430 (1901).

Dammer, Handb. anorg. Chem., 2 (2), 182 (1894); 4, 321 (1903).

4. Isomeric with the metaphosphates is a series of salts in which four of the six metals are replaceable:

5. Still another series exists, and in these five of the metallic atoms appear as ions 1:

It is noteworthy that the latter series contain the residue $[Na(PO_3)_6]$, which calls to mind the general complex radicle $[MX_6]$.

At present it is impossible to decide whether the polymerization exhibited by the phosphonitrile chlorides 2 and their derivatives, the metaphosphime acids, are of the same type as that displayed by the metaphosphates. For our knowledge of these compounds we have to thank Stokes. He showed that when a mixture of phosphorus pentachloride and ammonium chloride are distilled beyond the phosphonitrile chloride discovered by Liebig, a number of isomers are produced. The following table sets forth their empirical composition, etc.:

	Melting- point.	Boiling- point at 13 mm.	Boiling-point at 760 mm.
Triphosphonitrile chloride, (PNCl ₂) ₃ Tetraphosphonitrile chloride, (PNCl ₂) ₄ Pentaphosphonitrile chloride, (PNCl ₂) ₅ Hexaphosphonitrile chloride, (PNCl ₂) ₆ Heptaphosphonitrile chloride, (PNCl ₂) ₇ Polyphosphonitrile chloride, (PNCl ₂) _x	114° 123·5° 41° 91° -18° below red heat	127° 188° 223–224° 261–263° 289–294° decom- poses	256·5° 328·5° polymerizes ,,, decomposes

One of the most characteristic properties of these compounds is their tendency to polymerize. On heating to 250-350° they pass into a gelatinous mass of a very high molecular weight. The mass is elastic and insoluble in all indifferent solvents. On further heating, the mass decomposes and may be distilled, thus yielding all the above compounds. Consequently we have to do with a sort of genetic polymerization, the only example known as yet to inorganic chemistry.

¹ Lüdert, Zeitsch. anorg. Chem., 5, 15 (1894); Dammer, loc. cit.

² Amer. Chem. J., 17, 275 (1895); 19, 782 (1897).

On treating the first four phosphonitrile chlorides with water, the following decomposition takes place:

$$(PNCl2)x + 2xH2O = 2xHCl + [PN(OH)2]x$$

The products of this reaction are the metaphosphime acids, which again are polymerized, and Stokes has given them the following constitutions:

Trimetaphosphimeic acid

Tetrametaphosphimeic acid

From the hepta-chloride on, metaphosphime acids are no longer produced, but compounds containing one molecule of water more and to which Stokes has given chain-formulæ, e.g. heptameta-phosphime acid:

In the masterly work of Stokes are contained many observations which are of great value to structural inorganic chemistry, and on this account a fresh examination of these interesting compounds is greatly to be desired.

Some very interesting cases of polymerism have been brought to light by the researches on the polynuclear metallic amminocomplexes. Thus, a series of hexammintrioldicobalti salts are known which have the general formula²:

$$\begin{bmatrix} (\mathbf{H_3N})_3\mathbf{Co} & . & \mathbf{OH} \\ . & . & \mathbf{OH} \\ . & . & \mathbf{OH} \\ . & . & \mathbf{OH} \end{bmatrix} \mathbf{X_3}$$

These salts are coloured a beautiful brownish-red.

Zeitsch. anorg. Chem., 19, 38 (1899).
 Werner, Ber., 40, 4834 (1907).

The dodecamminhexoltetracobalti salts have the following formula 1:

$$\left[\text{Co} \left(\frac{\text{HO}}{\text{HO}} \text{Co} (\text{NH}_3)_4 \right)_3 \right] X_6$$

These salts, which are beautifully crystallized, are coloured brownish-black.

On comparing the following empirical formulæ it will be obvious that the salts belonging to this series are also polymeric:

Once more, the compounds

$$\begin{bmatrix} (H_3N)_4Co \\ \cdot \\ OH \end{bmatrix} \cdot \begin{bmatrix} Co(NH_3)_4 \end{bmatrix} Br_4 + 2H_2O \quad and \quad [(H_3N)_4Co_{OH_2}^{OH}] Br_2 \\ Octammin-diol-dicobalti bromide ^2 \qquad \qquad Hydroxo-aquo-tetrammin-cobalti bromide ^3 \end{bmatrix}$$

are polymerides, as is evident from a comparison of their empirical formulæ:

$$Co_2(OH)_2(NH_3)_8Br_4 + 2H_2O$$
 and $Co(OH)(NH_3)_4Br + H_2O$

And finally, in the chromium series we have, amongst others, the two polymeric compounds;

$$[(H_3N)_5Cr.OH.Cr(NH_3)_5](S_2O_6)_2 + 2H_2O \text{ and } \begin{bmatrix} Cr_{(NH_3)_5}^{OH} \end{bmatrix}S_2O_6 + H_2O \\ OH \\ Basic erythrochromdithionate ' \\ Enromdithionate ' \\ Chromdithionate ' \\ Chromdithionat$$

It is hardly necessary to add that the recognition of the cause of these isomeric phenomena marks a considerable advance in inorganic structural formulæ.

2. Co-ordination Isomerism.

In the earlier chapters it has been pointed out that metallic atoms can form complexes with the most varied components. Suppose that we have two different metallic atoms Me and Me', which possess this property to the same degree, and suppose,

¹ Werner, ibid., p. 2103.

² Werner, Ber., 40, 4434 (1907).

³ Werner, ibid., p. 4113.

⁴ Jörgensen, J. pr. Chem., (2) 45, 274 (1892).

⁵ Jörgensen, ibid., (2) 25, 418 (1882).

further, that two different components, A and A', are taken up by the metals, then the following variations are conceivable. Me can combine both with A and A', and Me' likewise, so that the complexes (MeA_x) and (MeA'_x), (Me'A_x) and (Me'A'_x) are formed. When the addition of A to Me and Me' gives rise to positive radicles, and when the addition of A' to Me and Me' yields negative radicles, then the four complexes can, by uniting together, produce the following pair of isomeric compounds:

$$(MeA_x).(Me'A'_x)$$

 $(MeA'_x).(Me'A_x)$

The following simple cases illustrate this :-

$$\left[\mathrm{Co}_{\mathrm{OH}_2}^{(\mathrm{NH}_3)_5}\right]\!\!\left[\mathrm{Cr}(\mathrm{CN})_6\right]\ \mathrm{and}\ \left[\mathrm{Cr}_{\mathrm{OH}_2}^{(\mathrm{NH}_3)_5}\right]\!\!\left[\mathrm{Co}(\mathrm{CN})_6\right]$$

and also the following pairs of isomers discovered by Pfeiffer:3

Because these compounds differ only in the components co-ordinated to the central atom, I have called this type of isomerism."

The following compounds are further illustrations:

¹ Braun, Annalen, 125, 183 (1863).

² Jörgensen, J. pr. Chem., (2) 30, 31 (1884); Pfeiffer, Annalen, 346, 42 (1906).

³ Pfeiffer, Annalen, 346, 28 (1906).

Pfeiffer, Zeitsch. anorg. Chem., 58, 307, 315 (1908).

⁵ Thomson, Ber., 2, 668 (1869).

⁶ Millon and Cornaille, Compt. rend., 57, 882.

[Zn(NH₃)₄]^{II}. [PtCl₄]^{II} Tetramminezinco-tetrachloroplatoate ¹ and $[Pt(NH_3)_4]^{II}$. $[ZnCl_4]^{II}$ Tetrammineplato-tetrachlorozincoate ²

further 3

As is obvious, these compounds can be considered as being produced by the reciprocal exchange of the groups linked to the central atom. But it is not necessary that all the groups should be transferred. An example will make the result of this clear. On combining triethylenediamincobalti salts, $[Coen_3]X_3$, with the blue potassium chromi oxalate, $[Cr(C_2O_4)_3]K_3 + 3H_2O$; and triethylenediaminechromi salts, $[Cren_3]X_3$, with potassium cobaltioxalate, $[Co(C_2O_4)_3]K_3 + 3H_2O$, the isomers 1 and 4 are obtained.

 $[\mathrm{Co}\;\mathrm{en}_3]^{\mathrm{III}}\cdot[\mathrm{Cr}(\mathrm{C_2O_4)_3}]^{\mathrm{III}}$

1. Triethylenediaminecobaltichromioxalate 5 $\begin{bmatrix} \mathbf{Co}_{2}^{\mathbf{C}_{2}\mathbf{O}_{4}}^{\mathbf{C}_{2}\mathbf{O}_{4}} \end{bmatrix}^{\mathbf{I}} \cdot \begin{bmatrix} \mathbf{Cr}_{(\mathbf{C}_{2}\mathbf{O}_{4})_{2}}^{\mathbf{en}} \end{bmatrix}^{\mathbf{I}}$

2. Oxalatodiethylenediaminecobaltiethylenediaminechromioxalate 6

 $\left[\mathbf{Co_{(C_2O_4)_2}^{en}} \right]^{\mathbf{I}} \cdot \left[\mathbf{Cr_{en_2}^{C_2O_4}} \right]^{\mathbf{I}}$

3. Oxalatodiethylenediaminechromiethylenediaminecobaltioxalate

 $[\mathbf{Co}(\mathbf{C}_2\mathbf{O}_4)_3]^{111} \cdot [\mathbf{Cr} \ \mathbf{en}_3]^{111}$

4. Triethylenediaminechromicobaltioxalate 8

But should from the acid radicle of compound 1 be transferred only one oxalate residue, then compound 2 would be formed. Experiment has confirmed this prediction. For Pfeiffer was able to prepare the compound from the oxalatodiethylene-

¹ Thomson, Ber., 2, 668 (1869).

² Buckton, Annalen, 84, 270.

³ Pfeiffer, ibid., 346, 28 (1906).

⁴ Pietsch, Inaug.-dissert., Zürich, 1907.

⁵ Pfeiffer, loc. cit.

⁶ Ibid.

⁷ Not yet known.

⁸ Pfeiffer, loc. cit.

⁹ Ibid.

diaminecobalti salts 1 and from a potassium salt, to which Schwarz 2 gave the formula

$$\left[\mathbf{Cr_{(C_2O_4)_2}^{en}}\right]\!K$$

Through the exchange of two of the oxalate residues in the acid radicle of compound 1, for two ethylenediamine molecules of the basic radicle, compound 3 ought to be produced. This compound, however, has not yet been prepared, because monethylenediaminecobalti salts are not yet known, but its preparation will certainly become possible.

In order that two compounds should be co-ordinate isomers it is not necessary for the central atoms of the positive and negative complexes to consist of different metals. Examples of this type of isomerism are known in great quantity, as may be seen from the following:

Hexammincobalti-hexanitrocobaltiate 5

$$\left[\begin{array}{c} \operatorname{Pt}^{\operatorname{Cl}}_{(\operatorname{NH}_3)_3} \end{array} \right]^{\operatorname{I}} \cdot \left[\operatorname{Pt}^{\operatorname{NH}_3}_{\operatorname{Cl}_3} \right]^{\operatorname{I}}$$
Chlorotriamminplato-amminetrichloroplatoate 4

$$\begin{bmatrix} \operatorname{Co}(\mathrm{NO_2})_2 \\ \operatorname{NH_3})_4 \end{bmatrix}^{\mathrm{I}} \cdot \begin{bmatrix} \operatorname{Co}(\mathrm{NH_3})_2 \\ \operatorname{Co}(\mathrm{NO_2})_4 \end{bmatrix}^{\mathrm{I}}$$
Dinitrotetrammincobaltidiammintetranitrocobaltiate 6

Pfeiffer and his pupils have lately described the following isomers:

$$\begin{split} & [Cr\,en_3]\,[Cr(C_2O_4)_3] \quad and \quad \Big[Cr^{en_2}_{C_2O_4}\Big] \Big[Cr^{(C_2O_4)_2}_{en}\Big] \\ & [Cr(NH_3)_6]\,[Cr(C_2O_4)_3] \quad and \quad \Big[Cr^{(NH_3)_4}_{C_2O_4}\Big] \Big[Cr^{(C_2O_4)_2}_{(NH_3)_2}\Big]^8 \\ & \Big[Cr^{(OH_2)_2}_{en_2}\Big] [Cr(C_2O_4)_3] + 2H_2O \quad and \quad \Big[Cr^{C_2O_4}_{en_2}\Big] \Big[Cr^{(OH_2)_2}_{(C_2O_4)_2}\Big] + 2H_2O \quad \end{split}$$

¹ Zeitsch. anorg. Chem., 21, 145 (1899).

² Schwarz, Über die Beziehungen zwischen Metallammoniaken und komplex Salzen. Inaug.-diss., Zürich, 1903.

³ Magnus, Pogg. Ann., 14, 242 (1828); Claus., Annalen, 107, 38 (1858).

⁴ Cossa, Ber., 23, 2503 (1890).

⁵ Jörgensen, Zeitsch. anorg. Chem., 5, 177 (1894).

d Jörgensen, ibid.

¹ Annalen, 342, 283 (1906).

[·] Ibid., 846, 28 (1906).

Stern, Inaug.-diss., Zürich, 1908.

To the same group also belong the following isomers, which are of more complicated constitution in that they are made up of a number of complex radicles:

$$\left[\operatorname{Pt}(\mathbf{NH}_{3})_{4}\right]^{\operatorname{II}}\cdot\left[\operatorname{Pt}_{\operatorname{Cl}_{3}}^{\mathbf{NH}_{3}}\right]_{2}^{\operatorname{I}}$$

Tetramminplato-amminetrichloroplatoate 1

$$\left[\mathrm{Co}(\mathrm{NH_3})_6\right]^{\mathrm{III}} \cdot \left[\mathrm{Co}_{(\mathrm{NO_2})_4}^{(\mathrm{NH_3})_2}\right]_3^{\mathrm{I}}$$

Hexammincobalti-diamminetetranitrocobaltiate 3

$$\left[\begin{array}{c} \operatorname{Pt}^{\operatorname{Cl}}_{(\operatorname{\mathbf{NH}}_3)_3} \right]_3^{\operatorname{I}} \cdot \left[\operatorname{PtCl}_4 \right]^{\operatorname{II}} \\ \operatorname{Chlorotriamminplato-tetra-} \\ \operatorname{chloroplatoate}^2 \end{array}$$

$$\left[\text{Co}_{(\mathbf{NH}_3)_4}^{(\mathbf{NO}_2)_2} \right]^{\text{I}} \cdot \left[\text{Co}_{(\mathbf{NO}_2)_6} \right]^{\text{III}}$$

Dinitrotetrammincobaltihexanitrocobaltiate

Two co-ordinative isomers corresponding to the formula

$$\mathbf{Hg}_{2}(\mathbf{CN})_{4}$$
. $2\mathbf{CS} < \mathbf{NH}_{2} + \mathbf{H}_{2}\mathbf{O}$

have been prepared and described by Kohlschütter.5

A peculiar case of co-ordinative isomerism is that in which the central atoms of the positive and negative radicles are the same, but of different valency. When the radicle with the higher valency transfers some of its groups to the other radicle, then this type of isomerism is brought about, thus:

Tetramminplato-hexachloroplateate ⁶

$$\left[\mathbf{Pt}^{\mathbf{Cl}_2}_{(\mathbf{NH}_3)_4}\right]^{\mathbf{II}} \cdot \left[\mathbf{PtCl}_4\right]^{\mathbf{II}}$$

Dichlorotetramminplatintetrachloroplateate 7

$$[PtPy_4]PtCl_6$$
 and $\Big[Pt^{Cl_2}_{Py_4}\Big]PtCl_4$ 8

The examples of co-ordinative isomerism which up to the present have been cited, are all drawn from molecular compounds. But valency compounds also display this type of isomerism, as Sabanejeff?

¹ Cossa, Ber., 23, 2503 (1890).

² Peyrone, Annalen, 51, 1 (1844); 55, 205 (1845); 61, 178 (1847); Cleve, K. Sv. Vet. Akad. Handl., 10, No. 93.

3 Jörgensen, Zeitsch. anorg. Chem., 5, 182 (1894).

4 Jörgensen, loc. cit.

5 Ber., 36, 1151 (1903).

6 Cossa, Gazzetta, 17, 1 (1887); Ber., 20, 462 (1887).

⁷ Cossa, Gazzetta, 17, 1 (1887).

8 Cossa, Zeitsch. anorg. Chem., 2, 186 (1892).

⁹ J. Russ. Phys. Chem. Soc., 30, 403, 415 (1899); 31, 375 (1899); Zeitsch. anorg. Chem., 17, 480.

has pointed out. He, however, called such isomers "Structural Isomers." This definition Hantzsch objected to, and proved that these isomers are only simpler examples of co-ordinative isomerism. Sabanejeff prepared the following compounds:

$$\left[\mathbf{N_{OH}^{H_3}}\right]^{\mathrm{I}} \cdot \left[\mathbf{PO_2H_2}\right]^{\mathrm{I}}$$

Hydroxylaminehypophosphite

$$\left[\mathbf{N_{OH}^{H_3}}\right]_2^{I} \cdot \left[\mathbf{S_2O_6}\right]^{II}$$

Hydroxylaminedithionate

$$[\mathbf{N_2H_5}]^{\mathrm{I}} \cdot [\mathbf{PO_3H_2}]^{\mathrm{I}}$$

Hydrazinephosphite

$$[N_2H_6]^{II} \cdot [PO_3H_2]_2^{II}$$

Acid hydrazinephosphite

$$[\mathbf{N_2H_5}]^{\mathrm{I}} \cdot [\mathbf{PO_4H_2}]^{\mathrm{I}}$$

Hydrazine phosphate

$$[\mathbf{N}_2\mathbf{H}_6]^{II}\cdot[\mathbf{PO_4H_2}]_2^I$$

Acid hydrazinephosphate

$$[\mathbf{N}_3\mathbf{H}_5]^{\mathrm{I}} \cdot [\mathbf{P}_2\mathbf{O}_6\mathbf{H}_3]^{\mathrm{I}}$$

Hydrazinehypophosphate

$$[NH_3OH]^1 \cdot [S_{O_2}^{NH_2}]^1$$

Hydroxylamine amidosulphonic acid

$$\big[\mathbf{NH_4}\big]^{\mathrm{I}} \cdot \big[\mathrm{PO_3H_2}\big]^{\mathrm{I}}$$

Acid ammonium phosphite

$$[\mathbf{NH_4}]_2^{\mathrm{I}} \cdot [\mathbf{S}_2 \mathbf{O}_8]^{\mathrm{II}}$$

Ammonium persulphate

$$[\mathbf{NH}_4]^{\mathrm{r}} \cdot \left[\mathbf{P}_{\mathrm{O}_3\mathrm{H}}^{\mathbf{NH}_2}\right]^{\mathrm{r}}$$

Acid ammoniumamidophosphite

$$[\mathbf{NH_4}]_2^{\mathbf{I}} \cdot [\mathbf{P_2O_6H_2}]^{\mathbf{II}}$$

Ammonium hypophosphate

$$[\mathbf{N}\mathbf{H}_3\mathbf{O}\mathbf{H}]^{\mathrm{I}} \cdot \left[\mathbf{P}_{\mathbf{O}_3}^{\mathbf{N}\mathbf{H}_2}\right]^{\mathrm{I}}$$

Hydroxylamine amidophosphorous acid

$[\mathbf{NH_3OH}]_2^{\mathbf{I}} \cdot [\mathbf{P_2O_6H_2}]^{\mathbf{II}}$ Hydroxylamine hypophosphate

 $[\mathbf{NH_4}]_2^{\mathbf{I}} \cdot [\mathbf{PO_3}]_2^{\mathbf{I}}$ Ammonium metaphosphate

$$[NH_4]^i \cdot [S_{O_3}^{NHOH}]^i$$

Ammonium oxyamidosulphonic acid $[\mathbf{N}_2\mathbf{H}_6]^{\mathrm{I}}\cdot[\mathbf{SO}_4]^{\mathrm{II}}$

Hydrazine sulphate

3. Hydrate Isomerism.

Closely related to co-ordination isomerism is a type which has been called "Hydrate Isomerism." Isomers of this type contain water molecules differently combined in the complex radicles.

The most beautiful example of hydrate isomerism is that furnished by chromium chloride. Three different hydrates of the formula $CrCl_3 + 6H_2O$ are known. One is greenish-blue, which dissolves giving a blue-violet solution, and two are green, which dissolve yielding green solutions. The greenish-blue and one of the green chlorides have been examined by Gubser² and the

² Ber., 84, 1601 (1901).

¹ Hantzsch, ibid., 19, 106 (1890).

author, and the remaining one Bjerrum ¹ discovered and described. In the aqueous solution of the greenish-blue chloride all three chlorine atoms are present as ions. This is shown by its electrical conductivity, cryoscopic determinations, and by its behaviour towards silver nitrate. This chloride consequently has the following formula: [Cr(OH₂)₆]Cl₃, and is completely analogous in its behaviour to hexamminechromi chloride, [Cr(NH₃)₆]Cl₃. In the solution of Bjerrum's chloride only two chlorine atoms are ionized, for it is only possible to precipite two-thirds of the chlorine with silver nitrate from a freshly prepared solution which has been acidified with nitric acid. The formula of this chloride is consequently

$$\left[\mathrm{Cr_{(OH_2)_5}^{Cl}}\right]$$
 $\mathrm{Cl_2} + \mathrm{H_2O}$

On the other hand, a freshly prepared solution of the author's green chloride contains only one ionized chlorine, and hence, bearing in mind the results obtained from the study of the metallic ammino-compounds, the following formula has been given to this chloride:

$$\left[\mathrm{Cr_{(OH_2)_4}^{Cl_2}}\right]$$
Cl + 2H₂O

The position of the two extra molecules of water has been determined from the ease with which they leave the molecule; from the fact that this exit does not affect the properties of the complex; and from the fact that the bromide of this chloride,

$$\left[\mathrm{Cr}^{\mathrm{Cl}_2}_{(\mathrm{OH}_2)_4} \right]$$
 Br

does not contain these extra molecules.

The following facts, then, have been determined. They cannot be linked to the dissociated chlorine ions, for derivatives of the chloride in which chloridion has been replaced correspond to the formula:

$$\Big[\mathrm{Cr}^{\mathrm{Cl}_2}_{(\mathrm{OH}_2)_4} + 2\mathrm{H}_2\mathrm{O}\Big]\mathrm{X}$$

Hence, although they do not exercise the same functions as the water in the hexahydrochloride, yet they must in some way belong to the chromium complex. Moreover, when it is borne in mind that

I Ibid., 39, 1599 (1906); and also Bjerrum, Studier over Kromiklorid (Kopenhagen, 1907).

the green-blue chloride has not superfluous water, that the chloride of Bjerrum has one extra molecule, and that the author's green chloride contains two extra molecules, then we arrive at the conclusion that the water molecules are linked to the non-ionized chlorine. The isomerism between the three chlorides therefore receives the following expression:

$$[\mathrm{Cr}(\mathrm{OH_2})_6]\mathrm{Cl}_3$$

$$\left[\mathrm{Cr_{(OH_2)_5}^{Cl}}\right]$$
Cl.

$$\begin{bmatrix} \operatorname{Cr}(\operatorname{OH}_2)_6 \end{bmatrix} \operatorname{Cl}_3 \qquad \begin{bmatrix} \operatorname{Cr}_{(\operatorname{OH}_2)_5}^{\operatorname{Cl} \cdot \operatorname{H}_2\operatorname{O}} \\ \operatorname{Cr}_{(\operatorname{OH}_2)_5}^{\operatorname{Cl} \cdot \operatorname{H}_2\operatorname{O}} \end{bmatrix} \operatorname{Cl}_2 \qquad \begin{bmatrix} \operatorname{Cl} \cdot \operatorname{H}_2\operatorname{O} \\ \operatorname{Cr}_{(\operatorname{OH}_2)_4}^{\operatorname{Cl} \cdot \operatorname{H}_2\operatorname{O}} \\ \operatorname{OH}_2\right)_4} \operatorname{Cl}_2$$

Blue hydrate of chromium chloride

Bjerrum's chloride

Green hydrate of chromium chloride

Similar relations are observed between the two hexahydrates of chromium bromide. The one has a blue and the other a green colour. Silver nitrate immediately precipitates all the bromine from the blue salt, while from a solution of the green bromide it is only partly precipitated. The isomerism in this case corresponds to the formulæ:

$$\big[\mathbf{Cr}(\mathbf{OH}_2)_6\big]\mathbf{Br}_3$$

Hexaquochromibromide Blue salt

$$\left[\mathrm{Cr}_{(\mathrm{OH_2})_4}^{\mathrm{Br_2}} + 2\mathrm{H_2O}\right]\!\mathrm{Br}$$

Dibromotetraquochromibromide Green salt

The following difficultly soluble derivative of the green series has been prepared:

$$\left[Cr_{(OH_2)_4}^{Br_2} + 2H_2O\right]^{I}\left[Co_{(NO_2)_4}^{(NH_3)_2}\right]^{I}$$

Hydrate isomerism is known also amongst the metallic amminocomplexes. Examples of this are:

$$\begin{bmatrix} \text{Cl} \\ \text{H}_2\text{O} \text{Co}(\text{NH}_3)_4 \end{bmatrix} \text{Cl}_2$$

Chloraquotetrammincobaltchloride 2 (violet)

$$/ \left[\frac{\text{Cl}}{(\text{H}_2\text{O})_2}\text{Co}(\text{NH}_3)_3 \right] \text{Br}_2$$

Chlorodiaquotriammincobalti bromide ' (violet)

$$[Cl2Co(NH3)4]Cl + H2O$$

Dichlorotetrammincobaltchloride 3 (green)

$$\begin{bmatrix} \text{Cl} \\ \text{Br} \end{bmatrix} \text{Co}_{(\text{NH}_3)_3}^{\text{OH}_2} \text{Br} + \text{H}_2\text{O}$$

Chlorobromoaquotriammincobalti bromide (brown)

Werner, Annalen, 322, 296 (1902).

² Jörgensen, Zeitsch. anorg. Chem., 17, 465 (1898); Werner and Klein, ibid., 14, 32 (1897).

³ Ber., 34, 1587 (1901).

Werner and Grün, ibid., 37, 4701 (1904).

$$\begin{bmatrix} \text{Cl}_{\text{H}_2\text{O}}\text{Co(NH}_3)_4 \end{bmatrix} \text{Br}_2 \\ \text{Chloroaquotetrammin-cobalti bromide}^1 \\ \text{(violet)} \end{bmatrix} \begin{bmatrix} \text{Br}_2\text{Co(NH}_3)_4 \end{bmatrix} \text{Cl} + \text{H}_2\text{O} \\ \text{Dibromotetrammin-cobalti chloride}^2 \\ \text{(deep green)} \end{bmatrix}$$

In the compounds in which the water is without the bracket, one acidic ion belongs to the complex; but in those compounds in which the water is within the bracket, the complex possesses two acidic ions. The last pair of these examples is of interest because they are also examples of the type of isomerism to be discussed next, i.e. Ionization isomers.

Pfeiffer 3 has drawn attention to the following group of isomers:

$$\begin{bmatrix} Cr_{(OH_{2})_{4}}^{Py_{2}} \end{bmatrix} Br_{3} + 2H_{2}O & and & \left[Br_{2}Cr_{(OH_{2})_{2}}^{Py_{2}} \right] Br + 4H_{2}O \\ \left[Cl_{2}Cr_{(OH_{2})_{2}}^{Py_{2}} \right] Cl & and & \left[Cl_{3}Cr_{OH_{2}}^{Py_{2}} \right] + H_{2}O \\ \left[en_{2}Cr_{(OH_{2})_{2}}^{(OH_{2})_{2}} \right] Br_{2} & and & \left[en_{2}Cr_{(OH_{2})_{2}} \right] Br_{3}^{-4} \end{bmatrix}$$

4 Pfeiffer, Zeitsch. anorg. Chem., 58, 322 (1908).

An interesting case of isomerism exists between the two salts:

$$O$$
 $<$ $^{PO_3Mg}_{PO_3Mg} + 3H_2O^5$ and $MgHPO_4 + H_2O^6$

- ⁵ Schwarzenberg, Ann. Chem. Pharm., 65, 146 (1848).
- ⁶ A. de Schulten, Compt. rend., 100, 877 (1885).

The former salt gives up all its water at 100°, while the latter at this temperature loses none.

4. Ionization Metamerism.

A peculiar type of isomerism, often met with in the metallic ammino-complexes and to be expected amongst the hydrates, is that in which compounds of the same composition yield different ions in solutions. Thus, two compounds are known which have the molecular formula Co(NH₃)₅Br.SO₄, and are consequently to be looked upon as formed by the addition of five molecules of ammonia to cobaltibromo sulphate. But in solution they are quite different.

¹ Jörgensen, J. pr. Chem., (2) 42, 216 (1900).

² Werner and Wolberg, Ber., 38, 992 (1905).

³ Ibid., 39, 1879 (1906).

The one is a reddish-violet colour, and gives in a freshly prepared solution no reaction for bromine ions, but does for the sulphate ion. On the other hand, the solution of the second red salt gives the reactions of bromidion, but not of the sulphate ion. Double decomposition with metallic salts and acids proves conclusively that solutions of the former compound contain the complex ion $\left[\operatorname{Co}_{(\mathrm{NH_3})_5}^{\mathrm{Br}}\right]^{++}$, while solutions of the latter contain the complex ion $\left[\operatorname{Co}_{(\mathrm{NH_3})_5}^{\mathrm{SO}_4}\right]^{+}$.

The following are further examples of this type of isomerism:

$$\left[\begin{array}{c} \text{Co}_{(\mathbf{NH}_3)_5}^{\mathbf{Br}} \\ \text{Bromopentammincobal} \end{array}\right]$$

Bromopentammincobalti sulphate ¹ (reddish-violet)

Nitratopentammincobalti sulphate 3

.
$$\left[C_{0}^{\mathbf{Br}}_{(\mathbf{NH_{3}})_{5}}\right]C_{2}O_{4}$$

Bromopentammincobalti oxalate *

$$\begin{bmatrix} {\rm Cl} {\rm Co(NH_3)_4} \end{bmatrix} {\rm Cl}$$

Chloronitrotetrammincobalti chloride (red)

$$\begin{bmatrix} \mathbf{Cl} \\ \mathbf{O_2N} \mathbf{Co} \ \mathbf{en_2} \end{bmatrix} \mathbf{Cl}$$

Chloronitrodiethylenediamincobalti chloride (fire-red)

$$\left[\mathrm{Co_{(NH_3)_5}^{SO_4}}\right]\mathrm{Br}$$

Sulphatopentammincobalti bromide² (red)

$$\left[\mathrm{Co}_{(\mathrm{NH_3})_5}^{\mathrm{SO_4}}\right]\!\mathrm{NO_3}$$

Sulphatopentammincobalti nitrate 4

$$\left[\mathrm{Co_{(NH_3)_5}^{C_2O_4}} \right]$$
 Br

Oxalatopentammincobalti bromide 6

Dichlorotetrammincobalti nitrite * (green)

Dichlorodiethylenediamincobalti nitrite 10 (green)

Jörgensen, J. pr. Chem., (2) 19, 49 (1879).

² Jörgensen, ibid., (2) 31, 262 (1885).

³ Jörgensen, ibid., (2) 23, 227 (1881).

Jörgensen, ibid., (2) 31, 262 (1885).

⁵ Jörgensen, ibid., (2) 19, 49 (1879).

Jörgensen, Zeitsch. anorg. Chem., 11, 418 (1896).

¹ Jörgensen, ibid., 17, 468 (1898).

Werner and Klein, ibid., 14, 33 (1897).

Werner, Ber., 34, 1733 (1901).

¹⁰ Jörgensen, J. pr. Chem., (2) 39, 1 (1889).

 $\begin{bmatrix} \text{Cl} \\ \text{O}_2 \text{N} \text{Co en}_2 \end{bmatrix} \text{NO}_2$ $[(O_2N)_2Co\ en_2]Cl$ Chloronitrodiethylenediamin-Dinitrodiethylenediamincobalti nitrite 1 cobalti chloride 2 (red) (yellowish-brown) Cl Co en₂ SCN NCS Co en₂ Cl $\begin{bmatrix} \text{Cl} \\ \text{NCS} \text{Co en}_2 \end{bmatrix} \text{NO}_2$ Chloronitrodiethylene-Thiocyanatonitro-Chlorothiocyanatodiaminecobaltidiethylenediaminediethylenediaminethiocyanide 3 cobaltidichloride 4 cobalti nitrite 5 (red) (red-brown) (brownish-violet) $\left[\frac{\mathrm{HO}}{\mathrm{Cl}}\mathrm{Pt}(\mathrm{NH_3})_4\right]\mathrm{SO_4}$ [HO O.S Pt(NH₃)₄]Cl Hydroxochlorotetrammin-Hydroxosulphatotetramminplate sulphate 6 plate chloride 6 $[\mathrm{Cl_2Pt}(\mathrm{NH_3})_4]\mathrm{Br_2}$ $[\mathrm{Br}_{2}\mathrm{Pt}(\mathbf{NH}_{3})_{4}]\mathrm{Cl}_{2}$ Dichlorotetramminplate-Dibromotetramminplatebromide 6 chloride 6 $[O_4S \cdot Pt(NH_3)_4](OH)_2$ $[(\mathrm{HO})_2\mathrm{Pt}(\mathrm{NH}_3)_4]\mathrm{SO}$ Sulphatotetramminplate-Dihydroxotetramminplatehydroxide 6 sulphate 6 $[\mathrm{Br_2Pt}(\mathrm{NH_3})_4]\mathrm{SO}_4$ $[SO_4Pt(NH_3)_4]Br_9$ Dibromotetramminplate-Sulphatotetramminplatesulphate 6 bromide 6

5. Salt Isomerism.

It is to be expected that the salts of tautomeric acids should appear as structural isomers; provided only that, like the organic esters of such acids, they do not dissociate electrolytically. Thiocyanic acid belongs to this group of acids and, as is well known, gives rise to the isomeric esters:

R.SCN and SCN.R.

Corresponding to these esters there exists two series of salts:

Me.S and SCN.Me

The first example of this type of isomerism was observed amongst

Werner, loc. cit.

² Ibid.

³ Ibid.

Werner and Gerb, Ber., 34, 1739 (1901).

⁵ Werner and Bräunlich, Zeitsch. anorg. Chem., 22, 154 (1899).

⁶ Cleve, K. Sv. Vet. Akad. Handl., 10, No. 93.

¹ Werner, Ber., 40, 765 (1907).

the dithiocyanatodiethylenediamine cobalt salts. Two series of these salts are known:

$$\begin{bmatrix} NCS : Coen_2 \end{bmatrix} X \qquad \text{and} \qquad \begin{bmatrix} SCN : Coen_2 \end{bmatrix} X \\ Normal dithiocyanato-diethylenediamine-cobalt salts 1} \qquad \text{and} \qquad \begin{bmatrix} SCN : Coen_2 \end{bmatrix} X$$

Their constitution may be satisfactorily determined from their oxidation products. The action of chlorine or bromine in the presence of water completely oxidizes the thiocyanide residue in the first salts, but, on account of its being more firmly linked to cobalt, the isothiocyanide residue, in the second salt, is unaffected by these reagents. It is interesting to note that just as the thiocyanide esters may be transformed into mustard oils, so is it possible to transform the dithiocyanato salts into diisothiocyanato salts. This transformation is brought about by repeatedly evaporating to dryness the aqueous solution of the salt, but not by simply heating a solution. A solution may be heated as often as desired without any change being noticeable.

Another case of salt isomerism the author and Zinggeler³ were able to prove exists among the nitrothiocyanatotetrammincobaltisalts.

If chloronitrotetrammincobalt chloride:

$$\begin{bmatrix} \text{Cl} \\ \text{NO}_2 \text{Co}(\text{NH}_3)_4 \end{bmatrix} \text{Cl}$$

is treated with potassium thiocyanide there results, as the author together with Klein has shown, a series of nitrothiocyanato-tetrammincobalti salts in which the thiocyanide residue is linked to cobalt by sulphur. On the other hand, if diaquotetrammincobalti salts, $[(H_2O)_2Co(NH_3)_4]X$, are treated with ammonium thiocyanide, a series of thiocyanatoaquotetrammincobalti salts are obtained,

$$\begin{bmatrix} SCN \\ H_2O \end{bmatrix} Co(NH_3)_4 X$$

in which the thiocyanide residue is linked to cobalt by nitrogen. Now, if a nitrite group is introduced into this complex, a compound

Werner and Bräunlich, Zeitsch. anorg. Chem., 22, 141 (1899).

Werner and Bräunlich, ibid., p. 127.

² Zinggeler, Über Rhodankobaltsalze, Dissertation, Zurich, 1902.

^{*} Zeitsch. anorg. Chem., 22, 91 (1899); and Werner, Ber. 40, 774 (1907).

results which is isomeric with Klien's, and which on oxidation yields nitropentammin salts. The isomerism in this series corresponds to the following formula:

$$\begin{bmatrix} O_2N \\ NCS : Co(NH_3)_4 \end{bmatrix} X \qquad \qquad \text{yields on oxidation} \qquad \begin{bmatrix} O_2N \\ Cl Co(NH_3)_4 \end{bmatrix} X \\ \text{Nitrothiocyanato-tetrammincobalt salts} \\ \text{(brown)} \\ \text{(Klein's series)} \end{bmatrix} X \qquad \qquad \begin{array}{c} \text{Chloronitro-tetrammincobalt salts} \\ \text{(brown)} \\ \text{(Klein's series)} \\ \end{bmatrix} X \qquad \qquad \begin{array}{c} \text{yields on oxidation} \\ \text{SCN} : Co(NH_3)_4 \end{bmatrix} X \qquad \qquad \begin{array}{c} \text{yields on oxidation} \\ \text{SCN} : Co(NH_3)_4 \end{bmatrix} X \\ \text{Isothiocyanato-tetrammincobalt salts} \\ \text{(yellowish red)} \\ \text{(Zinggeler 2 series)} \end{array} \qquad \begin{array}{c} \text{Nitropentammin-cobalt salts} \\ \text{cobalt salts} \\ \text{(Singgeler 2 series)} \\ \end{array}$$

It is important to note that oxidation with chlorine and bromine can always be used to determine the constitution of those metallic thiocyanides which yield metallic ammino-complexes which are stable towards acids. By using this reagent it was possible to prove that in the thiocyanides of chromium and platinum the thiocyanide residue is linked to the metal by sulphur, while, on the other hand, in the salts of thiocyanato-pentammin cobalt the residue is linked by nitrogen. Up to the present among the cobalt salts the following isothiocyanides are known:

$$\begin{bmatrix} \operatorname{Co^{NCS}_{(NH_3)_5}} \end{bmatrix} X_2^{-1} \qquad \begin{bmatrix} \operatorname{SCN}_{H_2O} \operatorname{Co(NH_3)_4} \end{bmatrix} X_2^{-2} \qquad \begin{bmatrix} \operatorname{SCN}_{O_2N} \operatorname{Co(NH_3)_4} \end{bmatrix} X^{-3} \\ \begin{bmatrix} \operatorname{SCN}_{SCN} : \operatorname{Coen}_2 \end{bmatrix} X^{-4} \quad \text{and} \quad \begin{bmatrix} \operatorname{SCN}_{SCN} : \operatorname{Copn}_2 \end{bmatrix} X^{-5}$$

and the following thiocyanides:

$$\begin{bmatrix} \mathbf{NCS}_{\mathbf{Co} \ \mathbf{en_2}} \end{bmatrix} \mathbf{X}^{6} \quad \begin{bmatrix} \mathbf{O_2N}_{\mathbf{Co}} \mathbf{Co(NH_3)_4} \end{bmatrix} \mathbf{X}^{7} \quad \mathbf{and} \quad \begin{bmatrix} \mathbf{NCS}_{\mathbf{Co} \ \mathbf{en_2}} \end{bmatrix} \mathbf{X}^{8}$$

Werner and Müller, Zeitsch. anorg. Chem., 22, 101 (1899); Werner, Ber., 40, 767 (1907).

² Werner, Ber., 40, 774 (1907).

3 Werner, ibid.

Werner and Bräunlich, Zeitsch. anorg. Chem., 22, 127 (1899).

5 Werner and Dave, Ber., 40, 789 (1907).

6 Werner, ibid., p. 768.

7 Werner, ibid.

Werner and Bräunlich, Zeitsch. anorg. Chem., 22, 127 (1899); Werner, Ber., 40, 766 (1907).

¹ Ber., 40, 767 (1907).

² Ibid., p. 774.

Hantzsch observed in the mercury salts of cyanuric acid isomerism of this type, and he therefore formulated the isomers as follows:

The oxygen salt is the product of the action of mercuric acetate or chloride on an aqueous solution of sodium cyanurate. The nitrogen salt is produced, as an anhydrous salt, when the free acid and these salts of mercury come together in solution irrespective of the temperature, but if the reaction is carried out at 100°, and alkali cyanurates replace the free acid, then the nitrogen salt is obtained as a dihydrate.

The difference in the two types of salt is seen in their behaviour towards alkali; the oxygen salt is immediately decomposed into the oxide of mercury and the alkali cyanurate, while the nitrogen salt is unattacked.

The oxygen salt is the unstable form and may be transformed into the nitrogen salt.

Nitrous acid, just like thiocyanic acid, forms salt isomers. Jörgensen, when working on the nitropentammincobalti salts,2

$$\left[\mathrm{Co}_{(\mathrm{NH_3})_5}^{\ \mathrm{NO_2}}\right]\!X_2$$

was the first to notice that such isomers exist. When these salts are produced from the aquopentammin salts intermediate ones are produced which are coloured a chamois-yellow, and which have been called the *iso*xanthrosalts, but the latter salts were so unstable that they could not be examined. The author, however, was able to prepare a more stable series of salts, corresponding to the *iso*xanthro

¹ Ber., 85, 2717 (1908).

² Jörgensen, Zeitsch. anorg. Chem., 5, 168 (1893); 19, 149 (1899); Werner, Ber., 40, 768 (1907).

Werner, ibid.

type, viz. two stereoisomeric series of dinitritodiethylenediamine-cobalti salts and one of dinitritodipyridinediamminecobalti salts:

$$= \begin{bmatrix} 1. & \text{ONO} \\ 2. & \text{ONO} \\ \text{Coen}_2 \end{bmatrix} X \quad \begin{bmatrix} 1. & \text{ONO} \\ 6. & \text{ONO} \\ \text{Coen}_2 \end{bmatrix} X \quad \text{and} \quad \begin{bmatrix} \text{ONO} \\ \text{ONO} \\ \text{Coen}_2 \end{bmatrix} X \\ \text{isomeric with the nitro-series:}$$

$$\begin{bmatrix} 1. & O_2N \\ 2. & O_2N \end{bmatrix} X \qquad \begin{bmatrix} 1. & O_2N \\ 6. & O_2N \end{bmatrix} Co \ en_2 \end{bmatrix} X \qquad and \qquad \begin{bmatrix} O_2N \\ O_2N \end{bmatrix} Co \begin{pmatrix} NH_3 \\ O_2 \end{pmatrix} X$$

The isomers are different in colour, those of the latter series are yellow to yellowish-brown, while those of the former are brickred. The difference between the series is again brought out by their behaviour towards mineral acids; for the former series are decomposed by acids, nitrous acid being liberated, while the latter are quite stable. The nitrito-salts are the labile isomers. For on keeping, most of them are completely transformed within forty-eight hours, and on heating to 60° to 70° the transformation is very soon complete.

6. Structural Isomerism.

Some workers look upon nitramide and nitrosohydroxylamine as inorganic structural isomerides:

Hantzsch 1 conceives these to be stereoisomers, thus:

A very pretty example of structural isomerism was discovered by Haga ² and shortly afterwards by Raschig. The hydrolysis of RSO_3 . ON: SO_3R produces salts with the formula RSO_3 . O.NH. SO_3R , which are called hydroxylamine-a- β -disulphonates, and are isomeric with the β - β -disulphonates, HO—N SO_3R , which have long been known.

¹ Annalen, 292, 340 (1896).

² Trans., 89, 240 (1906).

The following salts have been described:

KO₃S.O.NH.SO₃K, NH₄O₃S.ONH.SO₃NH₄, KO₃S.O.NK.SO₃K +2H₂O, NaO₃S.O.NH.SO₃Na and NaO₃S.O.NNa.SO₃Na +2H₂O.

The following salts are, according to Rosenheim and Meyer, to be considered as structural isomers of thiourea and ammonium thiocyanide:

7. Stereo-isomerism.

(a) Development of Space Formula.

Hydrates, metallic ammino-complexes, and many complex salts contain the radicle MeR₆, in which the six groups are bound directly to the central atom. Compounds containing this radicle appear as isomers, and the only way of explaining the experimental facts is by the help of a space formula. If the radicle is represented by a plane formula:

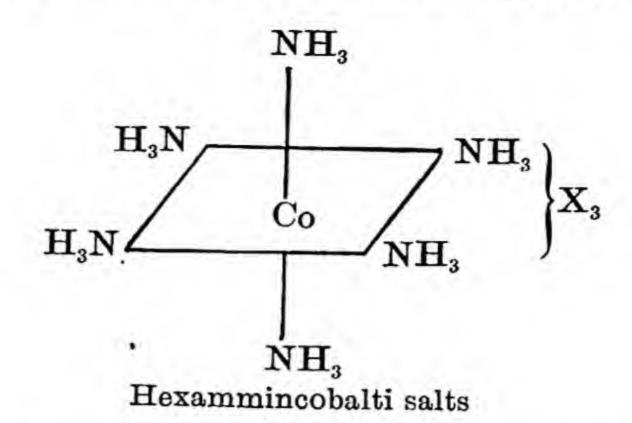
then, by substituting R' for R and thus obtaining the radicles

$$\mathbf{Me}_{\mathbf{R}_2}^{\mathbf{R'}_2}$$
 and $\mathbf{Me}_{\mathbf{R}_3}^{\mathbf{R'}_3}$

there ought to be produced the same number of di- and trisubstitution-products as in the case of benzene, i.e. three isomers.

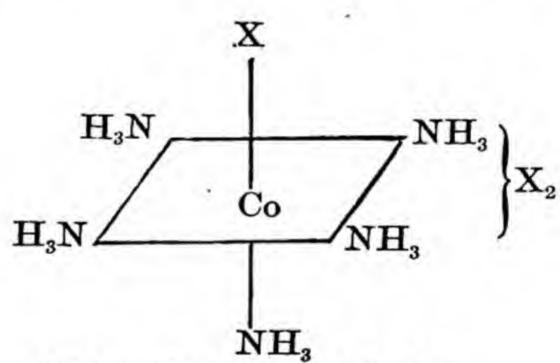
Up to the present, and in spite of much careful work, it has been
found impossible to obtain three isomers. More than two have
never been obtained. These facts are best explained by assuming that the groups are placed around the central atom at the
corners of a regular octahedron. Thus, the hexammincobalt
salts [Co(NH₃)₆]X₃ would be represented by the formula:

¹ Zeitsch. anorg. Chem., 49, 28 (1906).



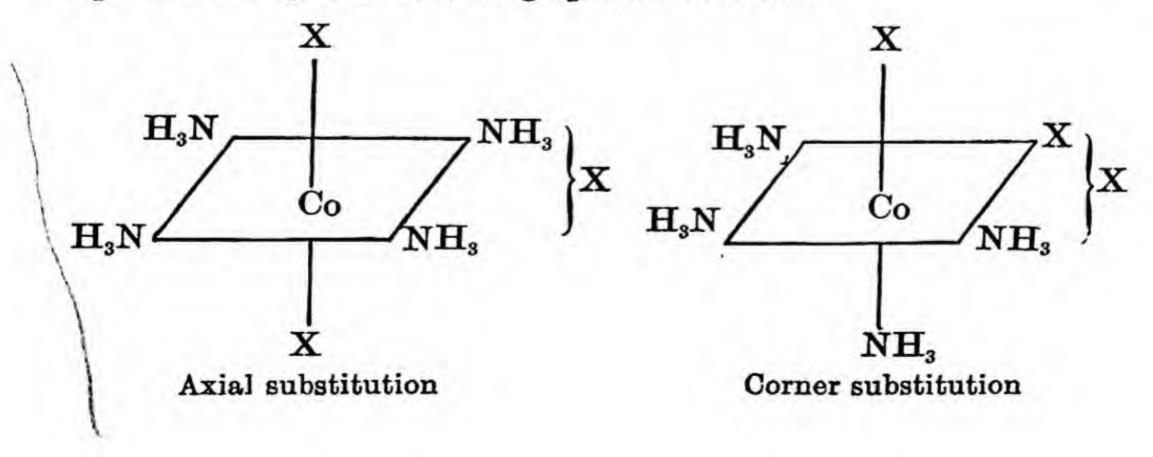
The following spacial formulæ are given, therefore, to the compounds resulting from the successive losses of ammonia.

In acidopentammin salts: $\left[\operatorname{Co}_{(\operatorname{NH}_3)_5}^X\right]X_2$, five of the corners of the octahedron are occupied by ammonia, and the sixth by an acid residue. Since all the corners of the octahedron have the same value, no isomeric compounds are to be expected, a fact expressed by the formula:



Acidopentammincobalti salts

But should a second acid residue be introduced into the acidopentammin salts, then two compounds are obtained which can be represented by the following spacial formulæ:



From this it follows that compounds containing the complex radicle: $\left[Me_{R_4'}^{R_2'}\right]$ are to be expected in two isomeric forms.

This theoretical deduction has received so much experimental confirmation that the accuracy of this spacial formula is no longer open to doubt. This type of isomerism is comparable to the geometrical isomerism of the ethylene-compounds. The isomerides with X at the ends of an axis of the octahedron correspond to the trans-forms, while those with X at the corners correspond to the cis-forms. This is easily seen on comparing the formulæ:

Inorganic stereo-isomerism of this description has been proved to exist amongst the cobalt, chromium, and platinum salts. The first example was discovered by Jörgensen, who prepared two isomeric series of dichlorodiethylenediamine cobalti salts of the formula $\begin{bmatrix} \operatorname{Co}_{en_2}^{Cl_2} \end{bmatrix} X$. He, however, supposed them to be structural isomers. The author, from a thorough examination of these salts, and because he was able to prepare many additional examples of isomerism, considers them to be stereo-isomers.

(b) Stereo-isomeric Cobalt Compounds.

1. Review.

The following cobalt salts, containing the radicle ${\rm Co}_{{
m R}_2}^{{
m A}_4}$, have been proved to exist in two isomeric series :

1.
$$[(O_2N)_2C_0(NH_3)_4]X^1$$

2. $[(O_8S)_2C_0(NH_3)_4]R^2$
3. $[Cl_2C_0 en_2]X^3$
4. $[Cl_2C_0 en_2]X^4$

¹ Gibbs, Proc. Amer. Acad., 10, 2 (1875); Jörgensen, Zeitsch. anorg. Chem., 5, 162 (1898).

² Hofmann and Reinsch, ibid., 16, 889 (1898); Werner and Grüger, ibid., p. 412.

Jörgensen, J. pr. Chem., (2) 41, 440 (1890).

Werner and Gerb, Ber., 84, 1739 (1901); Werner, ibid., p. 1733.

Life Charles	
5. $\begin{bmatrix} ON : O & Coen_2 \\ ON : O & Coen_2 \end{bmatrix} X^{1}$	9. $[(H_2O)_2Coen_2]X_3^5$
	10. $[(\mathbf{H}_{3}\mathbf{N})_{2}\mathrm{Coen}_{2}]\mathbf{X}_{3}^{6}$
6. $[(O_2N)_2Co\ en_2]X^2$ 7. $[BrCo\ en_2]X^3$	11. [Cl ₂ Copn ₂]X ⁷
	12. [Cl ₂ Co(NH ₃) ₄]X ⁸
8. $\begin{bmatrix} \text{HO} \\ \text{H}_2 \text{O} \end{bmatrix} \text{Coen}_2 X_2^4$	

¹ Werner, ibid., 40, 779 (1907).

² Werner and Humphrey, ibid., 34, 1720, 1726 (1901).

³ Jörgensen, loc. cit.

⁴ Werner, Ber., 40, 272 (1907).

⁵ Werner, *ibid.*, p. 262.

⁶ Werner, Annalen, 351, 65 (1907).

Werner and Fröhlich, Ber., 40, 2225 (1907).

⁸ Werner and Klein, Zeitsch. anorg. Chem., 14, 28 (1897); Werner, Ber., 40, 4817 (1907).

The isomerides in this series are chemically similar, for only one of the three acid residues is an ion. They differ, however, very characteristically in their colour; the dichloro and the dibromo salts of one series are green (the praseo-salts), those of the other are violet (violeo-salts). Since stereo-isomerism originally was observed only in those compounds which contained ethylenediamine, the opinion was expressed that the isomerism in these salts was due to the presence of the organic residue. The author, however, has been able to show that isomerism exists among the simple salts $[Cl_2Co(NH_3)_4]X$, in which a structural difference is excluded. In this way the accuracy of the stereochemical formulæ of such salts has been proved decisively.

2. Determination of Configuration.

As has been pointed out already, the octahedral configuration of the cobalt isomerides corresponds, with reference to those groups which determine the isomerism, to the space formula of ethylene isomerides, e.g. maleic and fumaric acids:

Now, one of the most important methods by which the configuration of organic geometric isomers is determined depends upon

THE CHEMICAL COMPOUNDS

the property of the cis-isomers of forming ring derivatives or of their production from such. The trans-forms do not give this reaction.

It was therefore to be anticipated that a similar difference would exist between the inorganic isomers. An examination confirmed this expectation, for it was found possible by a similar means to prove the configuration of the stereoisomeric cobalt salts.

The results of prolonged work of this description proved that the number of members in the ring have exactly the same influence on their formation in inorganic complexes as in organic compounds. Thus, it has been shown that ethylenediamine, propylenediamine, and trimethylenediamine form cobalt ammino-complexes very easily; but, on the other hand, tetramethylenediamine and pentamethylenediamine are unable to do so.

The steric cause of this is clear when the formulæ of the resulting atomic combinations are placed next one another:

In these cases rings containing four or five members are produced, while from tetramethylenediamine upwards rings must result which contain still more members, for the formation of which, as is well known, carbon compounds have no tendency. Similar observations have been made by Pfeiffer, and lately also by Tschugaeff, when preparing polymethylenediamine salts of nickel. Further support is obtained for this theory from the great stability of the dipyridyl- and o-phenanthroline metallic compounds, which have been examined by Blau; from the ease with which inorganic acetylacetonates are formed, the silicon and boron derivatives of which Dilthey has examined; and, finally, from the behaviour of the metallic isobutyradines, which Piloty and Schlenk have worked on. Everywhere it is found that the formation of rings in inorganic complexes conforms to the same laws which control their formation in the carbon and nitrogen compounds of organic

Ber., 36, 1065 (1903).

² Ibid., 39, 3197 (1906).

³ Monatsh., 19, 670 (1898).

⁴ Annalen, 341, 800 (1906).

Schlenk, Über Metall-isobutyradine und ihre Salze. Inaug. Dissertation, Munich, 1905.

chemistry. From this it may be concluded that spacial considerations play the same part in the formation of inorganic compounds as in the organic molecule. Hence it is highly probable that in carbonato-, oxalato-compounds, etc.:

$$A_4Me < O < CO$$
 and $A_4Me < O < CO < CO$

the oxygen atoms directly linked to the metallic atoms are not in the axial (i.e. trans) position on the octahedron, but rather in the corner (cis) position. In support of this, it may be mentioned that, in spite of many attempts, it has never been possible to prepare stereoisomeric carbonato- or oxalato-salts. Consequently the carbonato-compounds can be considered as cis-compounds, and as the starting-point configuration determinations. The author has used for this purpose the cobalt carbonato-salts and also the dioloctamminedicobalti salts, which likewise belong to the cis-compounds. On treating the latter with hydrochloric acid, 1, 2-dichlorotetrammin salts (violeo) are obtained, and these, in their turn, when treated with sodium nitrate, yield 1, 2-dinitrotetrammin salts (flavo). The latter, however, may be obtained directly from the carbonatotetrammin salts. The following diagram makes these genetic relations clear:

¹ Jörgensen, Zeitsch. anorg. Chem., 2, 282 (1892).

² Jörgensen, ibid., 5, 162 (1893).

³ Gibbs, Proc. Amer. Acad., 10, 2 (1875).

Werner, Ber., 40, 4817 (1907).

⁵ Gibbs and Genth, Researches on the Am. Cub. Bases, pp. 13 and 52 (1856);

$$\begin{bmatrix} (\mathbf{N}\mathbf{H}_3)_4\mathbf{Co} : \overset{\mathbf{OH}}{\mathbf{OH}} : \mathbf{Co}(\mathbf{N}\mathbf{H}_3)_4 \end{bmatrix} X_4$$

Octammin-diol-dicobalti salts 1

The carbonato-compounds also served as the starting-point for the ethylenediamine isomerides. The table on p. 260 gives expression to their genetic relations.

(c) Stereoisomeric Chromium Compounds.

(1) Review.

Pfeiffer and his pupils 'have discovered isomers among the diethy-lenediaminechromium compounds which are completely analogous to those of the cobalt compounds. On treating potassium chromium thiocyanide with ethylenediamine two isomeric series of dithiocyanidethylenediaminechromi thiocyanides are produced. From these, by replacing the thiocyanide residue by other groups, new isomers may be obtained. The following series of compounds have been prepared in this way:

 $\begin{array}{lll} & \left[\text{Cl}_2\text{Cr en}_2 \right] X,^1 & \left[(N\text{CS})_2\text{Cr en}_2 \right] X,^2 & \left[\text{Br}_2\text{Cr en}_2 \right] X,^2 & \left[(\text{H}_2\text{O})_2\text{Cr en}_2 \right] X_3,^3 \\ & \left[\begin{array}{c} \text{HO} \\ \text{H}_2\text{O} \end{array} \right] X_2,^3 \end{array}$

- 1 Ber., 37, 4255 (1904).
- ² Zeitsch. anorg. Chem., 56, 279 (1907).
- ³ Ibid., p. 261.

(2) Determination of Configuration.

Pfeiffer has determined the configuration of these isomers by making use of their genetic relations to the oxalato compounds:

$$\begin{bmatrix} OC - O \\ Cren_2 \end{bmatrix} X$$

or to the tetraethylenediamine-diol-dichromium salts:

$$\left[en_2Cr : {}_{OH}^{OH} : Cr en_2 \right] X$$

Rose, Untersuch. über ammoniakalische Kobaltverb., Heidelberg, 1871, p. 44; Vortmann, Ber., 10, 1454 (1878); 15, 1892 (1882); Werner and Klein, Zeitsch. anorg. Chem., 14, 38 (1897).

1 Werner, Ber., 40, 4434 (1907).

$$\begin{bmatrix} \text{OoC}_0^0 : \text{Coen}_t \end{bmatrix} X & \Rightarrow \begin{bmatrix} 1. \text{Ci} \text{Coen}_t \end{bmatrix} X & \Rightarrow \begin{bmatrix} 0.5^{\text{N}} \text{Coen}_t \end{bmatrix} X & \Rightarrow \begin{bmatrix} 0.5^{\text{N}} \text{Coen}_t \end{bmatrix} X \\ \text{Garbonatodischylene} \\ \text{diamine salts} \\ 1, 2-\text{dinnine salts} \\ 1, 3-\text{dinnine salts} \\ 1, 4-\text{dinnine salts} \\ 1, 4-$$

Both these salts, for reasons already discussed, are to be considered as cis-compounds. From these compounds only the violet dichloro-

and dibromo-salts have been prepared, the green isomers have been obtained by other methods. The violet salts must be consequently the cis-isomers, and it is very interesting to note that the stereo-isomeric chromium salts have exactly the same colours as the corresponding cobalt isomers. The table on p. 262 brings out the genetic relations between the stereoisomeric chromium compounds.

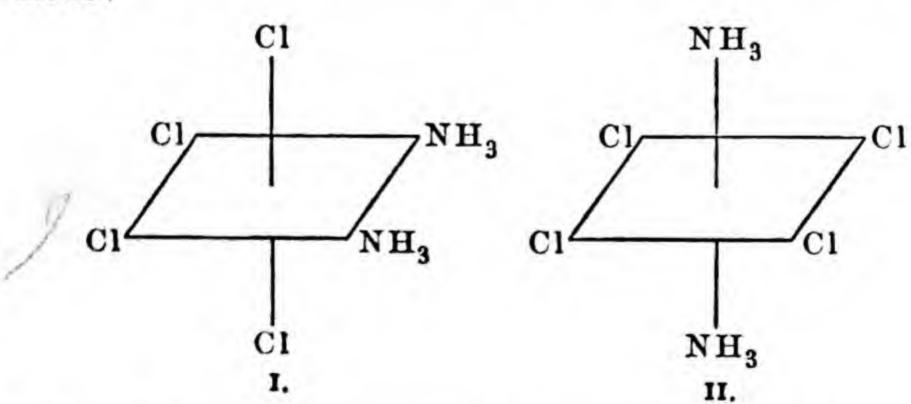
(d) Stereoisomeric Platinum Compounds.

1. Compounds of Tetravalent Platinum.

Stereoisomerism is also to be found amongst the platinum ammino-complexes. For two salts of the formula $(H_3N)_2PtCl_4^{-1}$ exist, viz. platinammin- and platinisemidiammin-chloride. Both of these compounds must have the constitution expressed by the formula:

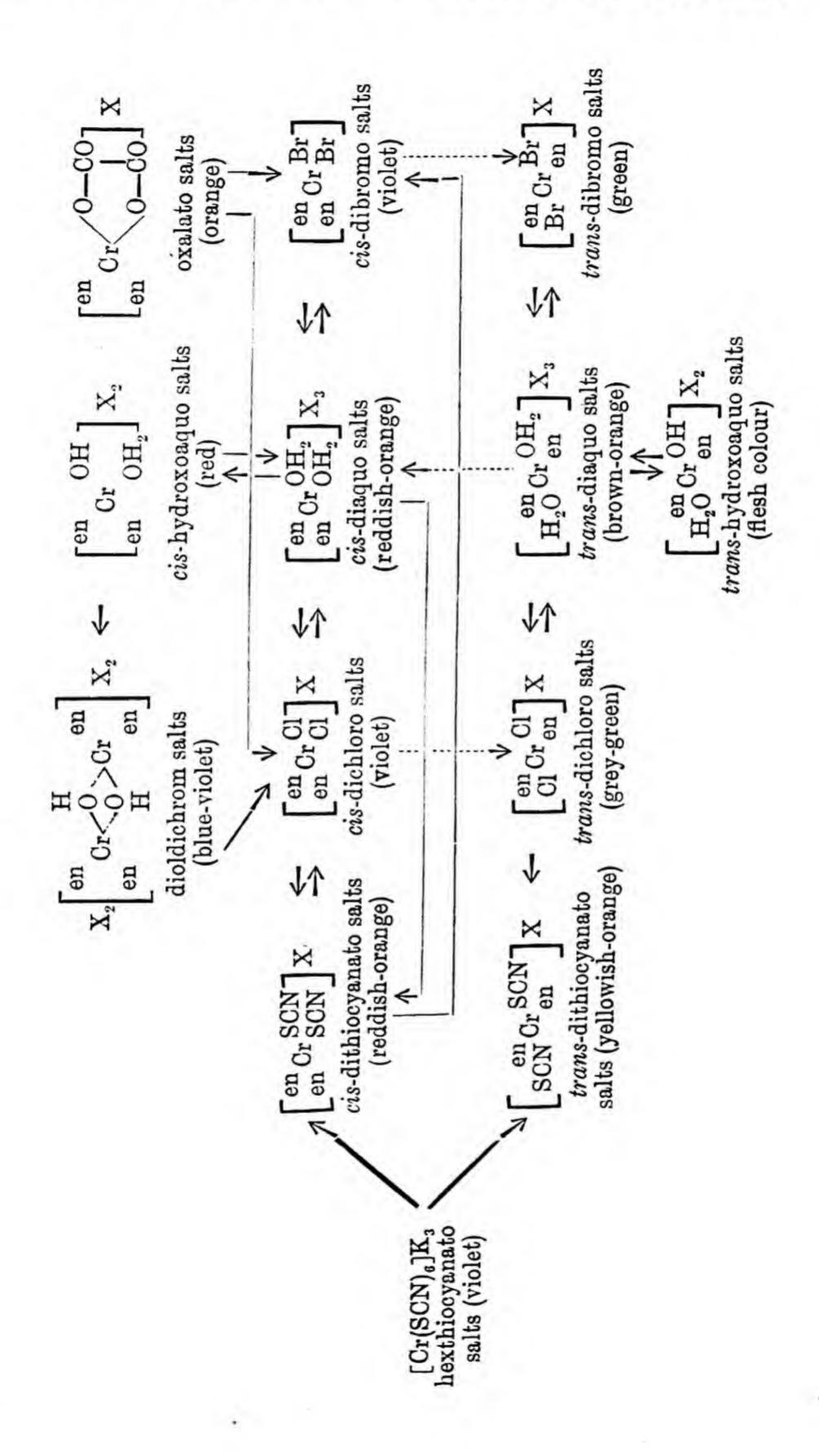
$$H_3N$$
 Pt
 Cl
 Cl
 Cl
 Cl

because neither of them contain ionic chlorine. Consequently, since structural isomerism is impossible, and since they do not belong to any of the other classes of isomerism already discussed, it follows that they must be stereoisomers. Moreover, they contain the characteristic radicle of stereoisomers, viz. $\mathrm{Me}_{R_4}^{R_2}$. The isomerism of these compounds is therefore expressed by the following spacial formulæ:



The platinammino-compounds are most probably represented by formula II., while formula I. will be that of the platinisemidiammin-compounds.

¹ Werner, Lehrbuch der Stereochemie, p. 349 (1904).



2. Compounds of Divalent Platinum.

(a) General.

As has been pointed out in the foregoing pages, a great many inorganic compounds exist in which the radicle MeR, plays the same part as the radicle MeR, in other compounds. Stereoisomeric derivatives of the radicle MeR, are known, and their special configuration is deduced from the following considerations.

If the groups in the radicle are symmetrically disposed in space as in carbon compounds, i.e. at the corners of a regular tetrahedron, isomerism would only be possible when all four groups are different. If, on the other hand, all the groups are in the same plane as the central atom, then isomerism is to be expected when one pair of groups are different from the remaining pair. The radicle would then be represented by the formula $\operatorname{Me} \frac{R'_2}{R_2}$, and the isomers by the special formulæ:

$$R$$
 Me
 R'
 R'
 R
 Me
 R'

The isomerism of the divalent platinum compounds is explained by this latter hypothesis. For two series of isomeric platinum compounds are known, which correspond to the general formula $(H_3N)_2PtX_2$, the chemical formation and physical behaviour of which prove that both compounds must have the same structural formula, viz.:

The names platosammin- and platosemidiammin have been given to the two series of salts, and the isomerism between, say, the chlorides is expressed by the following spacial formulæ:

The similarity between these formulæ and those of the ethylene geometrical isomerides is obvious, and hence formula I. is the cisconfiguration and formula II. the trans-configuration.

¹ Werner, loc. cit., p. 338.

(b) Review of the Stereoisomeric Compounds of Divalent Platinum.

The number of isomerides belonging to this group is very large.¹ Consequently only the most interesting groups will receive mention.

When chlorine is substituted by the residue SO₃H, the isomeric compounds corresponding to the formulæ

are obtained.

The same isomerism as is exhibited between semidiammine plato salts and platosammin salts is to be found among the phosphine, the alkylsulphide, and the alkylselenideplato-compounds. Rosenheim and Levy 2 have been able to prepare geometrical isomerides of this class from the phosphorustrichloroplato chlorides, thus:

$$\mathrm{Cl_2Pt}_{NH_2C_6H_5}^{\mathbf{P}(\mathrm{OC_2H_5})_3}\quad \mathrm{and}\quad \mathrm{Cl_2Pt}_{\mathbf{Py}}^{\mathbf{P}(\mathrm{OC_2H_5})_3}$$

The platodiammin compounds form the second group of amminoplato compounds in which geometrical isomerism has been observed. The isomerides in this group are represented by the following spacial formulæ:

$$\begin{bmatrix} \mathbf{H}_{3}\mathbf{N} & \mathbf{A}\mathbf{m} \\ \mathbf{H}_{3}\mathbf{N} & \mathbf{Pt} & \mathbf{A}\mathbf{m} \end{bmatrix} \mathbf{X}_{2} \quad \text{and} \quad \begin{bmatrix} \mathbf{H}_{3}\mathbf{N} & \mathbf{A}\mathbf{m} \\ \mathbf{A}\mathbf{m} & \mathbf{Pt} & \mathbf{N}\mathbf{H}_{3} \end{bmatrix} \mathbf{X}_{2}$$

These isomerides are formed by the substitution of two amine molecules for the acid residues in the platosemidiammin and platosammin salts. This process confers upon the acid residues ionic properties, and therefore the amine molecules must take up the position in the complex originally occupied by the acid residues.

The cis-isomeride is prepared by the action of pyridine on platosemidiammin chloride,3 thus:

$$\begin{array}{c|c}
\mathbf{H_{3}N} & \mathbf{Pt} & \mathbf{Cl} \\
\mathbf{H_{3}N} & \mathbf{Pt} & \mathbf{Cl} \\
\mathbf{H_{3}N} & \mathbf{Pt} & \mathbf{Py}
\end{array} \mathbf{Cl} \\
+ 2\mathbf{Py} = \begin{bmatrix} \mathbf{H_{3}N} & \mathbf{Py} \\ \mathbf{H_{3}N} & \mathbf{Py} \end{bmatrix} \mathbf{Cl_{2}} \\
cis-form$$

- ¹ A list of these compounds is given in the author's book on Stereochemistry, p. 338.
 - ² Zeitsch. anorg. Chem., 43, 34 (1904).
 - 3 Jörgensen, J. pr. Chem., 33, 510 (1886).

while the trans-isomeride is prepared from the platosammin chloride:

$$\begin{array}{c|c}
H_{3}N & Cl \\
Cl & Pt \\
NH_{3} & + 2Py = \begin{bmatrix} H_{3}N & Py \\
Py & NH_{3} \end{bmatrix}Cl_{2} \\
trans-form
\end{array}$$

The number of isomerides belonging to this class is also very large, for no fewer than nine series of isomeric salts are known, e.g. two isomeric series of dipyridinediamminplato salts, of dianiline-diamminplato salts, of diethylaminediamminplato salts, etc.

(c) Further Stereoisomeric Compounds.

It is very probable that the isomeric salts of silicontungstic acid and tungsten silicic acid are stereoisomers.² Both acids are octabasic and have the following constitution:

They therefore have the following steric formulæ:

8. Valency Isomerism.

Valency isomerism is brought about when it is possible for certain of the molecular components to be linked to a central atom by either of the types of valency. In one of the isomerides a certain radicle may be linked to the central atom by an auxiliary valency, while in the other isomeride the same radicle may be linked by a principal valency. On this account the author suggests that this type of isomerism be called "Valency Isomerism." According

² Marignac, Ann. Chim. Phys., (4) 3, 5 (1864).

A list of these isomerides is given by the author in his book on Stereochemistry, p. 342.

to Sand 1 this type of isomerism is to found in the two series of nitrosopentammin salts, which correspond to the following bimolecular formula: $[(NO)_2[Co(NH_3)_5]_2]X_4$. The salts belonging to one series are black, while those belonging to the other are red, and their difference in constitution is expressed by formulæ

$$X_{2}(NH_{3})_{5}Co...O=N$$
 $X_{2}(NH_{3})_{5}Co...O=N$
 $X_{2}(NH_{3})_{5}Co$
 $X_{2}(NH_{3})_{5}Co$
 $X_{2}(NH_{3})_{5}Co$

An examination of the isomeric series discovered by Jörgensen, i.e. rhodo² and erythro salts,³ has revealed that these salts are valency isomerides. From the results of experiment they have been given the following constitutional formulæ:

$$Cr(NH_3)_5]X_3$$
 $Cr(NH_3)_5]X_3$ OH $O \cdots HX$ $Cr(NH_3)_5]X_2$ $Cr(NH_3)_5]X_2$ $Cr(NH_3)_5]X_2$ Rhodo salts Erythro salts

The rhodo salts react neutral, the erythro salts strongly acid. On heating erythro bromide at 100° for some time it is transformed into rhodobromide. From the rhodo salts basic acids may be obtained, which react strongly alkaline and on standing in solution pass into basic erythro salts, which display no further basic properties.

These changes may be graphically represented as follows:

3 Jörgensen, loc. cit.

¹ Ber., 36, 1440 (1903); Sand and Genssler, Annalen, 329, 194 (1903).

² Jörgensen, J. pr. Chem., (2) 25, 321, 398 (1882); (2) 45, 279 (1892).

A very interesting case of valency isomerism is to be found among the esters of sulphurous acid. The principal valency compounds

have long been known, but the compound

$$_{\mathrm{O}}^{\mathrm{C}}$$
 $_{\mathrm{CH}_{3}}^{\mathrm{CH}_{3}}$

has been prepared only lately by Briner.2

9. Unexplained Isomeric Phenomena.

Locke and Edwards³ state that potassium ferricyanide may appear in two isomeric forms, which differ from each other in their chemical reactions. This case of isomerism has received no further attention. A fresh examination is to be desired, since the observations made by these workers are insufficient to class this isomerism.

Howe has lately drawn attention to the isomerism existing among the halogen salts of ruthenium. On boiling a very dilute solution of ruthenium chloride with hydrochloric acid and alcohol, making it alkaline, and then evaporating till crystallization sets in, deep red crystals of the formula $\left[\mathrm{Ru}_{\mathrm{Cl}_{5}}^{\mathrm{OH}_{2}}\right]\mathrm{R}_{2}$ are obtained, which at 140° lose their water.

Both the hydrated and anhydrous aquochlororutheniates are isomeric with the ordinary chlororutheniate. The corresponding aquobromorutheniates also have been prepared. The aquo-salts in solution are darkened in colour by the action of chlorine or iodine, and compounds with the general formula $[RuX_6]R_2$, e.g. $[RuCl_6]R_2$, are formed. These compounds are different from those obtained by Antony, by melting ruthenium with NaOH and KClO₃, so that it appears that we have to do with a case of isomerism.

A peculiar type of isomerism has been observed by Jorgensen

¹ Carius, Annalen, 110, 209 (1859); 111, 96 (1859); 114, 142 (1860); Rosenheim and Liebknecht, Ber., 31, 405 (1898); 38, 1298 (1905).

³ Briner, Arch. Sci. phys. nat., Oct. and Nov. (1907).

¹ Amer. Chem. J., 21, 193 (1898).

J. Amer. Chem. Soc., 26, 543, 942 (1904).

and Sörensen¹ when working on tetrammineplato-tetrachloroplatoate. This salt is green in its usual modification, and is consequently known as the "green salt of Magnus." Under certain conditions Jörgensen and Sörensen have obtained it as a deep red coloured salt. It is not yet decided to which class of isomerism this phenomenon belongs.

¹ Zeitsch. anorg. Chem., 48, 441 (1906).

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